Higher roots of the Schrödinger equation

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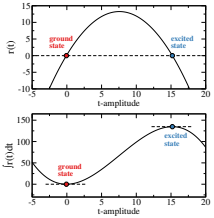
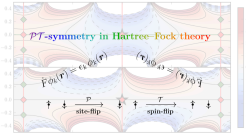
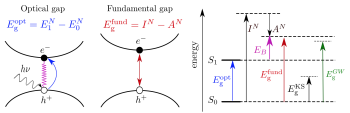
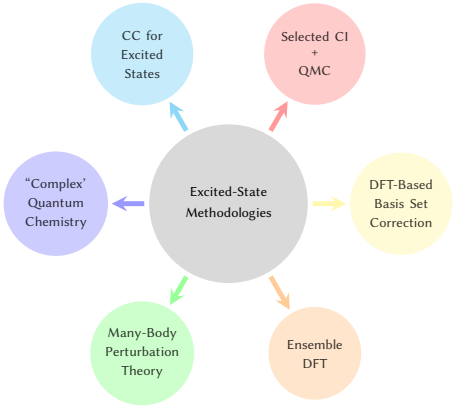
NHISS2021: Light-Matter Interaction: Theory meets Experiment

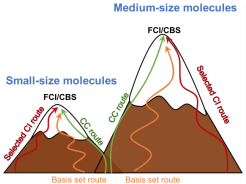
General overview of our research group

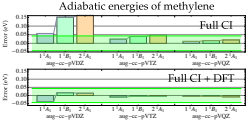


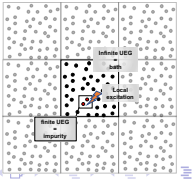












Selected CI or how to create new methods with new acronyms

"SCI+PT2 methods provide near full CI (FCI) quality energies with only a small fraction of the determinants of the FCI space"

- CIPSI (Malrieu, Evangelisti, Angeli, Spiegelman, Giner, Caffarel, Scemama, etc)
- Semistochastic Heat-bath CI (Sharma & Umrigar)
- Adaptive sampling CI (Evangelista & Tubman)
- Incremental CI (Zimmerman)
- Iterative CI (Liu & Hoffmann)
- FCIQMC (Alavi & Booth)
- ...

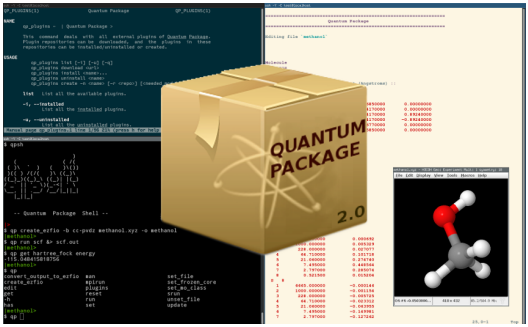
One selected CI (SCI) algorithm to rule them all

CIPSI = CI using a Perturbative Selection made Iteratively

- Developed in Toulouse many (many) years ago
  Huron, Malrieu & Rancurel, JCP 58 (1973) 5745
- Based on old idea by Bender and Davidson, and Whitten and Hackmeyer
  Bender & Davidson, Phys. Rev. 183 (1969) 23
  Whitten & Hackmeyer, JCP 51 (1969) 5584
- CIPSI (and SCI methods in general) has been recently resurrected!
  Giner, Scemama & Caffarel, CJC 91 (2013) 879
  Giner, Scemama & Caffarel, JCP 142 (2015) 044115
- CIPSI $\approx$ deterministic version of FCIQMC
  Caffarel et al., Recent Progress in Quantum Monte Carlo (2016) Chap. 2, 15-46.

Selected CI methods

"SCI+PT2 methods provide near full CI (FCI) quality energies with only a small fraction of the determinants of the FCI space"

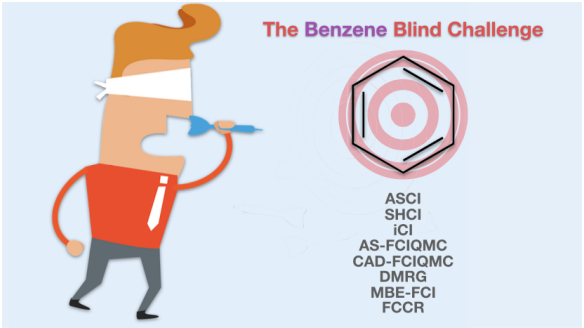


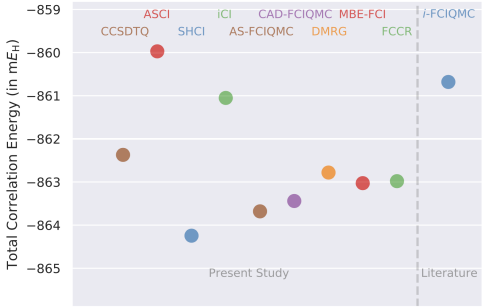
"Quantum Package 2.0: An Open-Source Determinant-Driven Suite of Programs", Garniron et al., JCTC 15 (2019) 3591

Anthony Scemama

Michel Caffarel

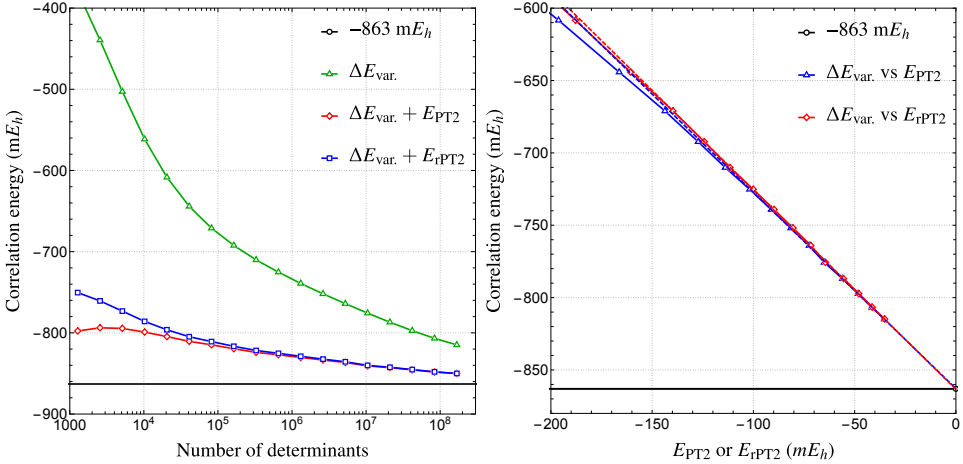
The Benzene Blind Challenge: Frozen-core correlation energy (cc-pVDZ)





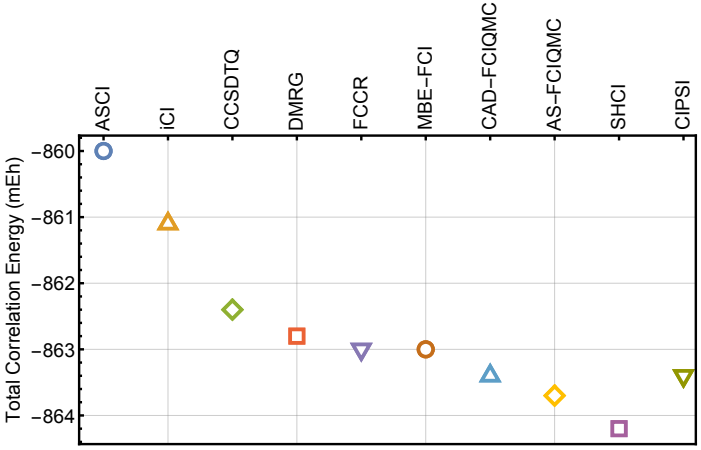
Eriksen et al. JPCL 11 (2020) 8922

Performance of CIPSI for C_6H_6/cc-pVDZ (1)



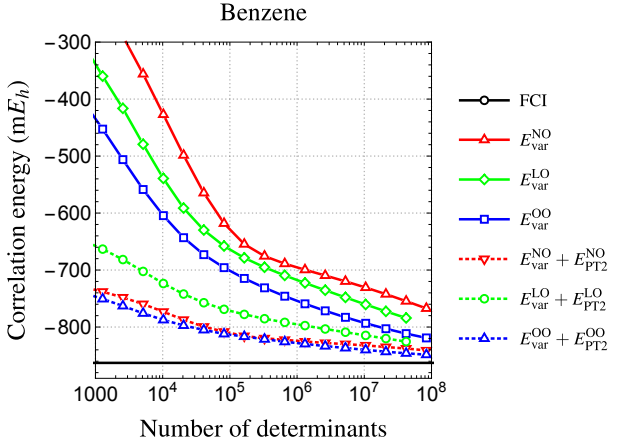
Loos, Damour & Scemama JCP 153 (2020) 176101

Performance of CIPSI for C_6H_6/cc-pVDZ (2)



Loos, Damour & Scemama JCP 153 (2020) 176101

Orbital-optimized CIPSI for C_6H_6/cc-pVDZ (and many others)



Damour et al. JCP 155 (2020) 176101

Yann Damour (PhD)

Toward a systematic improvement of the fixed-node approximation in diffusion Monte Carlo for solids—A case study in diamond

Cite as: J. Chem. Phys. **153**, 184111 (2020); https://doi.org/10.1063/5.0021036
Submitted: 06 July 2020 . Accepted: 12 October 2020 . Published Online: 11 November 2020

Anouar Benali, Kevin Gasperich, Kenneth D. Jordan, Thomas Applencourt, Ye Luo, M. Chandler Bennett, Jaron T. Krogel, Luke Shulenburger, Paul R. C. Kent, Pierre-François Loos, Anthony Scemama, and Michel Caffarel

See also Scemama et al. JCP 153 (2021) 174107 for a range-separated approach in molecules

Work by Prof Piecuch and his group

JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

Is Externally Corrected Coupled Cluster Always Better Than the Underlying Truncated Configuration Interaction?

Ilias Magoulas, Karthik Gururangan, Piotr Piecuch,* J. Emiliano Deustua, and Jun Shen

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High-level coupled-cluster energetics by merging moment expansions with selected configuration interaction

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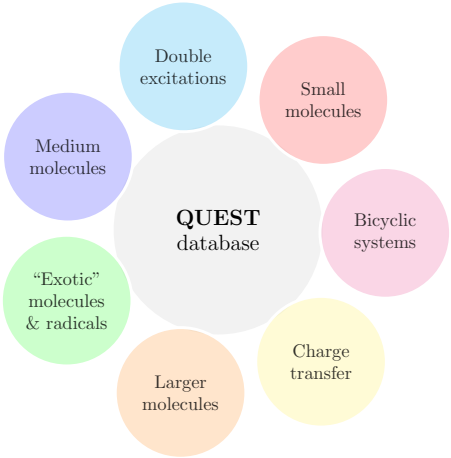
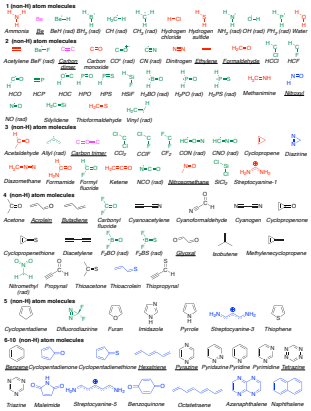
Karthik Gururangan, J. Emiliano Deustua, Jun Shen, et al.

Highly-accurate excitation energies: The QUEST project (1)

"The aim of the QUEST project is to provide to the community a large set of highly-accurate excitation energies for various types of excited states"



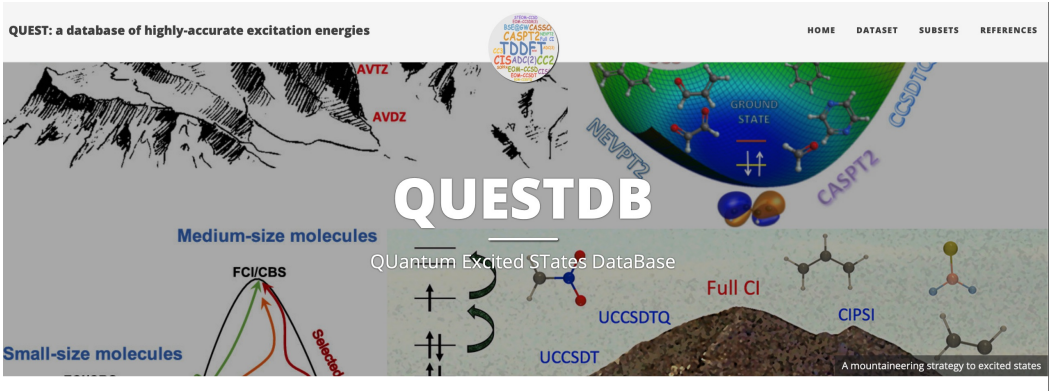


Mika Veril (PhD)

Martial Boggio-Pasqua

Denis Jacquemin

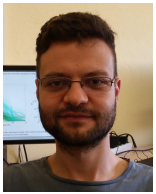
Highly-accurate excitation energies: The QUEST project (2)



Véril et al. WIREs Comput. Mol. Sci. 11 (2021) e1517

https://lcpq.github.io/QUESTDB_website/

Coupled-cluster theory for excited states



Fábris Kossoski
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Antoine Marie
(Master student)

Anthony Scemama
(CNRS)

Michel Caffarel
(CNRS)

Coupled-cluster theory

- 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*

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

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

$$\Psi_{\text{CI}} = (\hat{1} + \hat{T})\Psi_0 = (\hat{1} + \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_n)\Psi_0 \tag{6}$$

CC energies

- Schrödinger equation

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

- (Projected) Traditional CC energy (polynomial complexity)

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

- Variational CC energy (factorial complexity)

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

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

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

Traditional pair CCD (TpCCD)

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

$$\hat{T}\,|\Psi_0\rangle = \sum_{ia} t_{i\bar{i}}^{a\bar{a}}\,|\Psi_{i\bar{i}}^{a\bar{a}}\rangle = \sum_{ia} t_i^a\,|\Psi_{i\bar{i}}^{a\bar{a}}\rangle \tag{13}$$

- TpCCD energy

$$E_{\mathrm{TpCCD}} = \langle\Psi_0|\hat{H}|\Psi_0\rangle + \sum_{ia} t_i^a\,\langle ii|aa\rangle \tag{14}$$

- TpCCD residual

$$\begin{aligned} r_i^a = {} & \langle ii|aa\rangle + 2(f_a^a - f_i^i)t_i^a - 2\sum_j \langle jj|aa\rangle\, t_j^a t_i^a - 2\sum_b \langle ii|bb\rangle\, t_i^b t_i^a \\ & - 2(2\,\langle ia|ia\rangle - \langle ia|ai\rangle)t_i^a + 2\,\langle ii|aa\rangle\, t_i^a t_i^a \\ & + \sum_b \langle aa|bb\rangle\, t_i^b + \sum_j \langle ii|jj\rangle\, t_j^a + \sum_{jb} \langle jj|bb\rangle\, t_j^a t_i^b \end{aligned} \tag{15}$$

- Update amplitudes

$$t_i^a \leftarrow t_i^a - \frac{r_i^a}{2f_a^a - 2f_i^i} \quad \text{quasi-Newton algorithm} \tag{16}$$

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]

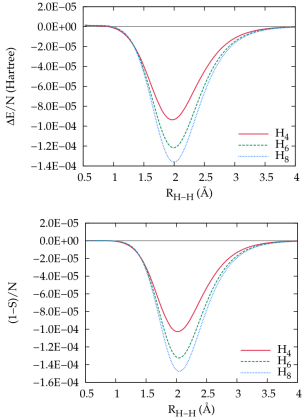


FIG. 3. Dissociation of equally spaced hydrogen chains. Top panel: Differences between DOCI and pCCD energies (ΔE, defined in Eq. (27)) per electron pair. Bottom panel: Deviations in the overlap ($1 - S$, with S defined in Eq. (28)) per electron pair.

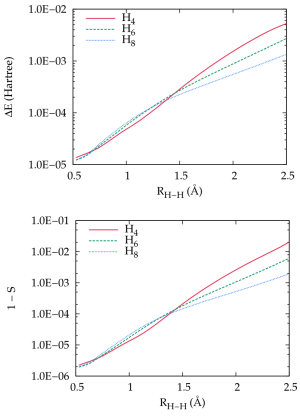


FIG. 4. Dissociation of equally spaced hydrogen chains in the canonical RHF basis rather than the pCCD-optimized basis used elsewhere. Top panel: Differences between DOCI and pCCD energies (ΔE, defined in Eq. (27)). Bottom panel: Deviations in the overlap ($1 - S$, with S defined in Eq. (28)).

Targeting excited states at the CC level

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

Equation-of-motion (EOM) formalism

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

Krylov, Annu Rev Phys 59 (2008) 433

"Ground state" formalism

There is more than one solution!!

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

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

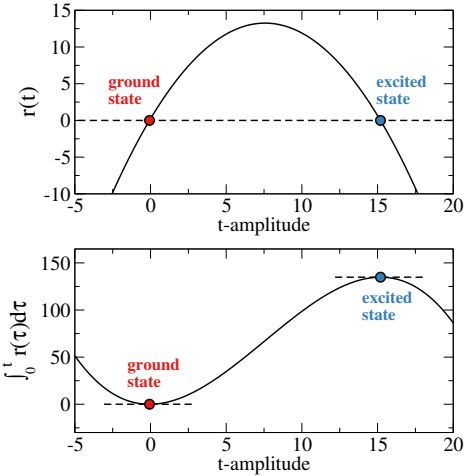
Example: TpCCD for He/6-31G with h = HOMO and l = LUMO

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

Residual and curvature

$$r(t) = \langle hh|ll\rangle + \Big(2f_l^l - 2f_h^h - 4\langle hl|hl\rangle + 2\langle lh|hl\rangle + \langle ll|ll\rangle + \langle hh|hh\rangle\Big)t - \langle ll|hh\rangle\, t^2 \quad (17)$$

$$r'(t) = 2f_l^l - 2f_h^h - 4\langle hl|hl\rangle + 2\langle lh|hl\rangle + \langle ll|ll\rangle + \langle hh|hh\rangle - 2\langle ll|hh\rangle\, t \quad (18)$$



Newton-Raphson algorithm to target excited states

$$\boxed{t_i^a \leftarrow t_i^a - \sum_{jb} (\boldsymbol{J}^{-1})_{ia,jb} r_j^b \quad \text{Newton-Raphson algorithm}} \tag{19}$$

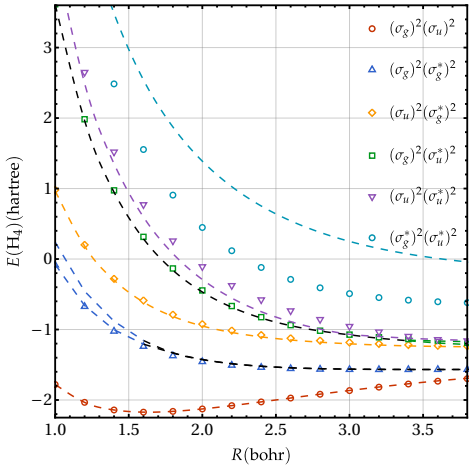
Elements of the exact Jacobian matrix for TpCCD

$$\begin{aligned} J_{ia,jb} = \frac{\partial r_i^a}{\partial t_j^b} = & \left[2f_a^a - 2f_i^i - 4\langle ia|ia\rangle + 2\langle ia|ai\rangle \right] \delta_{ij}\delta_{ab} \\ & + \left[\langle aa|bb\rangle - \langle jj|aa\rangle\, t_i^a + (1-2\delta_{ab}) \sum_{k\neq i} \langle kk|bb\rangle\, t_k^a \right] \delta_{ij} \\ & + \left[\langle ii|jj\rangle - \langle ii|bb\rangle\, t_i^a + (1-2\delta_{ij}) \sum_{c\neq a} \langle jj|cc\rangle\, t_i^c \right] \delta_{ab}. \end{aligned} \tag{20}$$

Kossoski, Marie, Scemama, Caffarel & Loos JCTC 17 (2021) 4756

NB: Same strategy works for VCC [Marie, Kossoski & Loos 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

$$\tilde{E}(\hat{T},\hat{\kappa}) = \langle \Psi_0 | \underbrace{(\hat{I}+\hat{Z})}_{\text{de-excitation operator}} e^{-\hat{T}} e^{-\hat{\kappa}} \hat{H} e^{\hat{\kappa}} e^{\hat{T}} | \Psi_0 \rangle \tag{21}$$

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

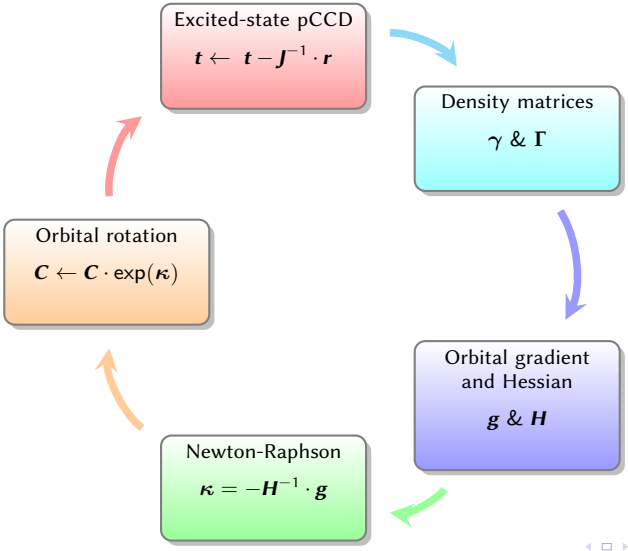
Updating the orbital coefficients

$$\tilde{E}(\boldsymbol{\kappa}) \approx \tilde{E}(\mathbf{0}) + \boldsymbol{g}\cdot\boldsymbol{\kappa} + \frac{1}{2}\boldsymbol{\kappa}^{\dagger}\cdot\boldsymbol{H}\cdot\boldsymbol{\kappa} \quad \Rightarrow \quad \boxed{\underbrace{\boldsymbol{C}}_{\text{new coefficients!}} \leftarrow \boldsymbol{C}\cdot e^{\boldsymbol{\kappa}} \quad \text{with} \quad \boldsymbol{\kappa} = -\boldsymbol{H}^{-1}\cdot\boldsymbol{g}} \tag{22}$$

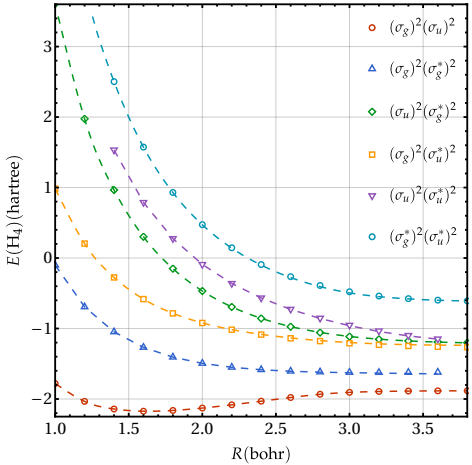
$$\text{Density matrices } \boldsymbol{\gamma} \ \& \ \boldsymbol{\Gamma} \quad \Rightarrow \quad \underbrace{g_{pq}}_{\text{gradient}} = \left.\frac{\partial \tilde{E}(\boldsymbol{\kappa})}{\partial \kappa_{pq}}\right|_{\boldsymbol{\kappa}=\mathbf{0}} \qquad \underbrace{H_{pq,rs}}_{\text{Hessian}} = \left.\frac{\partial^2 \tilde{E}(\boldsymbol{\kappa})}{\partial \kappa_{pq}\partial \kappa_{rs}}\right|_{\boldsymbol{\kappa}=\mathbf{0}} \tag{23}$$

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



Lowest doubly-excited state of CH^+

molecule	method	ΔE (eV)	$\Delta\Delta E$ (eV)
CH^+[1]	Δoo-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	$+0.23$

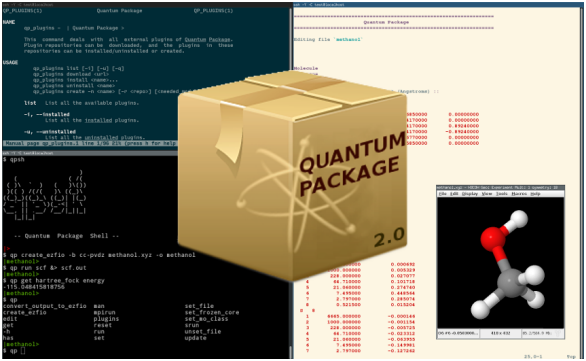
[1] Basis set and geometry taken from Olsen et al. CPL 154 (1989) 380
[2] Results from Olsen et al. CPL 154 (1989) 380
[3] Results from Kowalski & Piecuch, CPL 347(2001) 237
[4] Results from Boguslawski, JCTC 15 (2019) 18
[5] Results from Christiansen et al. JCP 103 (1995) 7429

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

molecule	method	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 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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