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Excited states from pCCD and DOCI

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https://lcpq.github.io/pterosor

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- CC wave function

$$\Psi = e^{\hat{T}}\Phi \qquad \text{where } \Phi \text{ is a reference wave function} \tag{1}$$

- Excitation operator

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_N \tag{2}$$

- Exponential *ansatz*

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

- Singles

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

- Doubles

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

- FCI wave function

$$\Psi = (\hat{1} + \hat{T})\Phi = (\hat{1} + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots)\Phi \tag{6}$$

- Schrödinger equation

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle \;\Rightarrow\; \hat{H}e^{\hat{T}}\,|\Phi\rangle = Ee^{\hat{T}}\,|\Phi\rangle \;\Rightarrow\; \underbrace{e^{-\hat{T}}\hat{H}e^{\hat{T}}}_{\bar{H}\,=\,\text{similarity transform}}\,|\Phi\rangle = E\,|\Phi\rangle \tag{7}$$

- Variational CC energy (factorial complexity)

$$E_{\text{VCC}} = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\Phi|e^{\hat{T}^\dagger}\hat{H}e^{\hat{T}}|\Phi\rangle}{\langle\Phi|e^{\hat{T}^\dagger}e^{\hat{T}}|\Phi\rangle} \geq E_{\text{FCI}} \tag{8}$$

- Projected CC energy

$$\boxed{E_{\text{CC}} = \langle\Phi|\bar{H}|\Phi\rangle = \frac{\langle\Phi|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi\rangle}{\langle\Phi|e^{-\hat{T}}e^{\hat{T}}|\Phi\rangle}} \tag{9}$$

- Amplitude equation for single amplitudes

$$\langle \Phi_i^a | \bar{H} | \Phi \rangle = 0 \quad \Rightarrow \quad t_i^a \tag{10}$$

- Amplitude equation for double amplitudes

$$\langle \Phi_{ij}^{ab} | \bar{H} | \Phi \rangle = 0 \quad \Rightarrow \quad t_{ij}^{ab} \tag{11}$$

- Amplitude equation for *n*-tuple amplitudes

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

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

$$\hat{T}\,|\Phi\rangle = \sum_{ia} t_i^a \left|\Phi_{\bar{i}\bar{i}}^{a\bar{a}}\right\rangle \tag{13}$$

- pCCD energy and amplitude equation

$$E = \langle\Phi|\hat{H}|\Phi\rangle + \sum_{ia} t_i^a \langle ii|aa\rangle \tag{14}$$

$$\begin{aligned} 0 = {} & \langle ii|aa\rangle + 2(f_{aa} - f_{ii})t_i^a - 2\sum_j \langle jj|aa\rangle\, t_j^a t_i^a - 2\sum_b \langle ii|bb\rangle\, t_i^b t_i^a \\ & - 2(2\langle ia|ia\rangle - \langle ia|ai\rangle)t_i^a + 2\langle ii|aa\rangle\, t_i^a t_i^a \\ & + \sum_b \langle aa|bb\rangle\, t_i^b + \sum_j \langle ii|jj\rangle\, t_j^a + \sum_{jb} \langle jj|bb\rangle\, t_j^a t_i^b \end{aligned} \tag{15}$$

- *"Bézout's number gives an upper bound to the number of solutions of a set of polynomial equations"*

$$B = \prod_{i}^{N_{\text{eq}}} d_i \tag{16}$$

- For pCCD, Bézout's number is 2^{OV} where O and V are the number of occupied and virtual orbitals

pCCD vs DOCI: Ground state [Henderson et al. JCP 141 (2014) 244104]

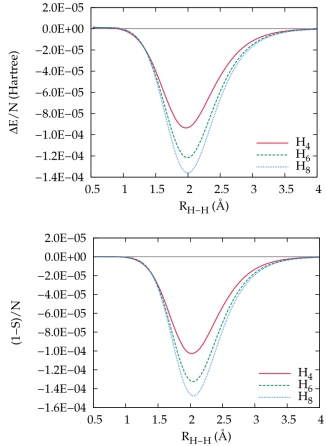


FIG. 3. Dissociation of equally spaced hydrogen chains. Top panel: Differences between DOCI and pCCD energies (ΔE, defined in Eq. (27)) per electron pair. Bottom panel: Deviations in the overlap ($1 - S$, with S defined in Eq. (28)) per electron pair.

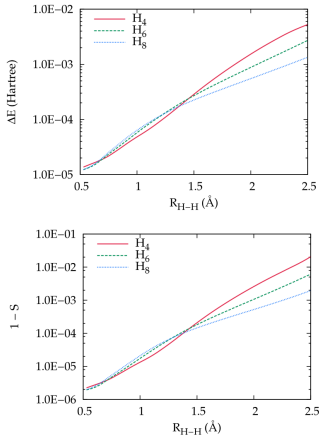
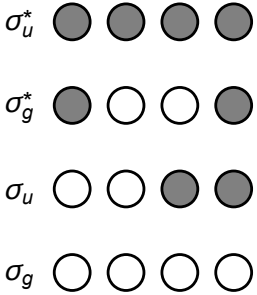
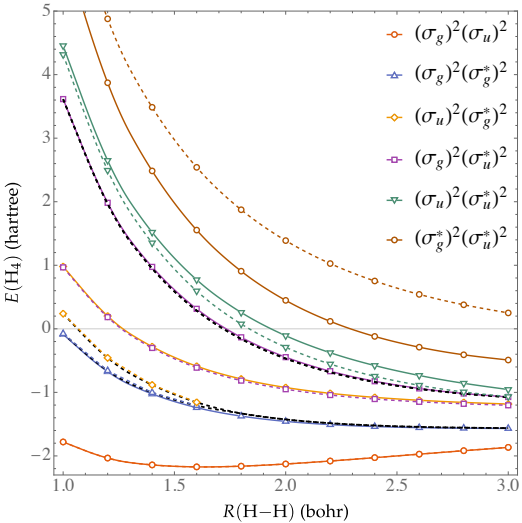


FIG. 4. Dissociation of equally spaced hydrogen chains in the canonical RHF basis rather than the pCCD-optimized basis used elsewhere. Top panel: Differences between DOCI and pCCD energies (ΔE, defined in Eq. (27)). Bottom panel: Deviations in the overlap ($1 - S$, with S defined in Eq. (28)).


σ_u^*
σ_g^*
σ_u
σ_g


$(\sigma_g)^2(\sigma_u)^2$
$(\sigma_g)^2(\sigma_g^*)^2$
$(\sigma_u)^2(\sigma_g^*)^2$
$(\sigma_g)^2(\sigma_u^*)^2$
$(\sigma_u)^2(\sigma_u^*)^2$
$(\sigma_g^*)^2(\sigma_u^*)^2$
$E(H_4)$ (hartree)
R(H−H) (bohr)
5
4
3
2
1
0
−1
−2
1.0
1.5
2.0
2.5
3.0