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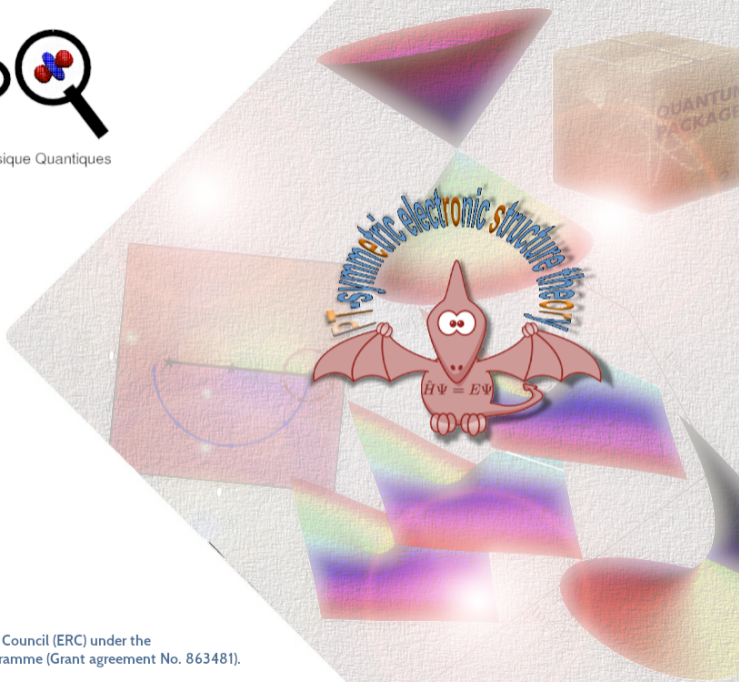
What can't CIPSI do?

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



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- ▶ **Green:** reference/variational/internal wave function (zeroth-order or model space)
- ▶ **Red:** perturbations or external wave function (first-order or perturbative space)

$$\begin{array}{l} \text{internal space } |I\rangle \\ \text{perturbations } |\alpha\rangle \end{array} \left\{ \begin{array}{|c|c|} \hline \mathbf{H}^{(0)} & \mathbf{h}^\dagger \\ \hline \mathbf{h} & \mathbf{H}^{(1)} \\ \hline \end{array} \right.$$



1. Define a (zeroth-order) *reference* wave function:

$$|\Psi^{(0)}\rangle = \sum_{I \in \mathcal{D}} c_I |I\rangle \qquad E^{(0)} = \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle}$$

2. Generate *external determinants*:

$$\mathcal{A} = \{(\forall I \in \mathcal{D}) (\forall \hat{T} \in \mathcal{T}_1 \cup \mathcal{T}_2) : |\alpha\rangle = \hat{T}|I\rangle\}$$

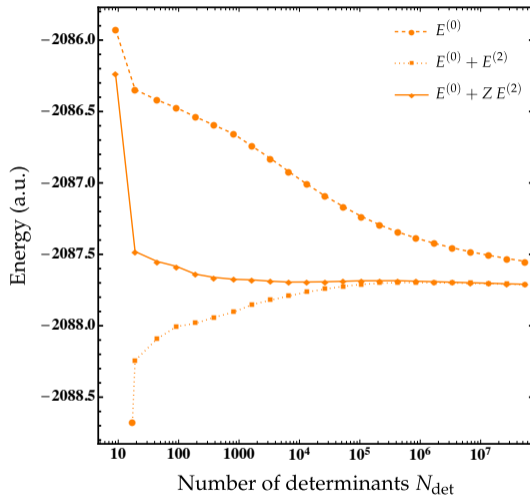
3. Second-order perturbative contribution of each $|\alpha\rangle$:

$$\delta E(\alpha) = \frac{|\langle \Psi^{(0)} | \hat{H} | \alpha \rangle|^2}{E^{(0)} - \langle \alpha | \hat{H} | \alpha \rangle}$$

4. Select $|\alpha\rangle$ with largest $\delta E(\alpha)$ and add them to \mathcal{D}
5. Diagonalize \hat{H} in $\mathcal{D} \Rightarrow$ update $|\Psi^{(0)}\rangle$ and $E^{(0)}$
6. Iterate



Ground state of Cr_2 in cc-pVQZ: full-valence CAS(28e,198o)



Garniron et al., JCTC 15 (2019) 3591



How do we know how far we are from the “true” FCI?

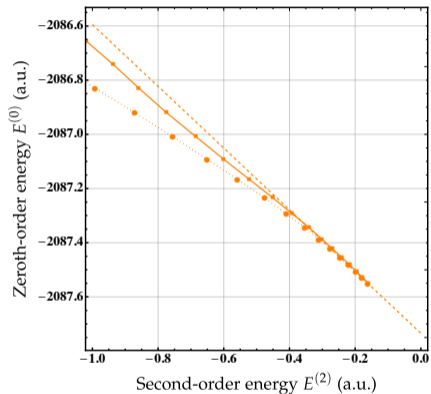
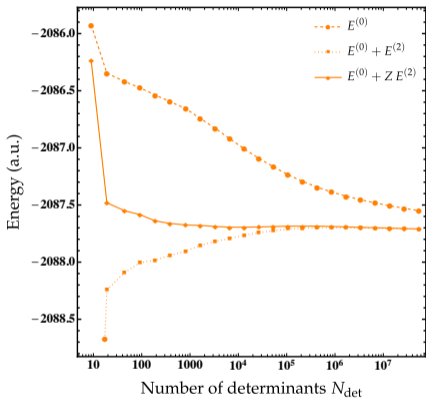
- ▶ Second-order Epstein-Nesbet correction:

$$E^{(2)} = \sum_{\alpha} \delta E(\alpha)$$

- ▶ $|\alpha\rangle$'s with largest $\delta E(\alpha)$ have been added to $\Psi^{(0)}$ previously
⇒ only small contributions remaining
- ▶ \mathcal{A} increases with \mathcal{D}
⇒ a *very large* number of *very small* contributions
- ▶ In practice, we use a semi-stochastic algorithm to compute $E^{(2)}$
⇒ *much faster!!*
Garniron, Scemama, Loos & Caffarel, JCP 147 (2017) 034101
- ▶ We *linearly extrapolate* to $E^{(2)} = 0$ to reach the FCI limit (exFCI)



Ground state of Cr_2 in cc-pVQZ: full-valence CAS(28e,198o)



Garniron et al., JCTC 15 (2019) 3591



At a given CIPSI iteration, the SCI+PT2 energy is given by

$$E = E^{(0)} + E^{(2)}$$

Let us introduce the following energy-dependent second-order self-energy

$$\Sigma^{(2)}[E] = \sum_{\alpha} \frac{\langle \alpha | \hat{H} | \Psi^{(0)} \rangle^2}{E - \langle \alpha | \hat{H} | \alpha \rangle} \quad \text{with} \quad \Sigma^{(2)}[E^{(0)}] = E^{(2)}$$

Brillouin-Wigner perturbation theory tells us

$$E = E^{(0)} + \Sigma^{(2)}[E]$$

Assuming that $\Sigma^{(2)}[E]$ behaves linearly for $E \approx E^{(0)}$

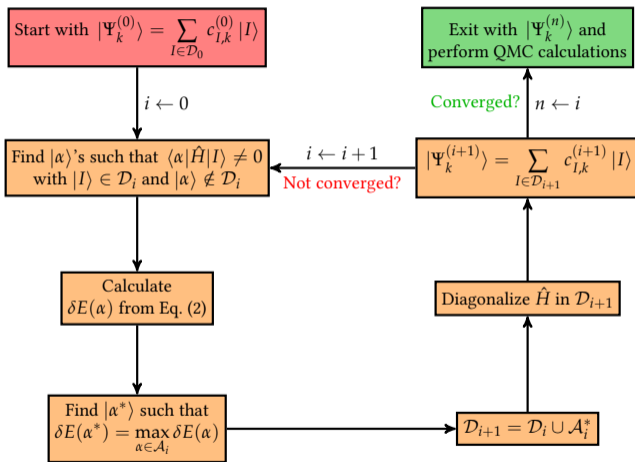
$$\Sigma^{(2)}[E] \approx \Sigma^{(2)}[E^{(0)}] + (E - E^{(0)}) \left. \frac{\partial \Sigma^{(2)}[E]}{\partial E} \right|_{E=E^{(0)}}$$

This yields

$$E = E^{(0)} + \Sigma^{(2)}[E^{(0)}] + (E - E^{(0)}) \left. \frac{\partial \Sigma^{(2)}[E]}{\partial E} \right|_{E=E^{(0)}} = E^{(0)} + Z E^{(2)} \quad \text{with} \quad Z = \left[1 - \left. \frac{\partial \Sigma^{(2)}[E]}{\partial E} \right|_{E=E^{(0)}} \right]^{-1}$$



CIPSI algorithm for excited states



$$\delta E(\alpha) = \sum_k^{N_{\text{states}}} \frac{c_{\alpha k}}{\max_I c_{Ik}^2} \langle \Psi_k^{(i)} | \hat{H} | \alpha \rangle,$$

with

$$c_{\alpha k} = \frac{\langle \Psi_k^{(i)} | \hat{H} | \alpha \rangle}{\langle \Psi_k^{(i)} | \hat{H} | \Psi_k^{(i)} \rangle - \langle \alpha | \hat{H} | \alpha \rangle}.$$



$$Hc - Ec = \begin{pmatrix} \mathbf{H}^{(0)} & \mathbf{h}^\dagger \\ \mathbf{h} & \mathbf{H}^{(1)} \end{pmatrix} \begin{pmatrix} \mathbf{c}^{(0)} \\ \mathbf{c}^{(1)} \end{pmatrix} - E \begin{pmatrix} \mathbf{c}^{(0)} \\ \mathbf{c}^{(1)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

internal space $ I\rangle$	$\mathbf{H}^{(0)}$	\mathbf{h}^\dagger
perturbers $ \alpha\rangle$	\mathbf{h}	$\mathbf{H}^{(1)}$

$$\Rightarrow \mathbf{c}^{(1)} = -(\mathbf{H}^{(1)} - EI)^{-1} \mathbf{h} \mathbf{c}^{(0)}$$

Effective Hamiltonian: $\mathbf{H}_{\text{eff}} = \mathbf{H}^{(0)} + \Delta$ Dressing term: $\Delta = \mathbf{h}^\dagger \mathbf{c}^{(1)}$

Approximation #1 (Bk method): $\Delta = \mathbf{h}^\dagger (EI - \mathbf{D}^{(1)})^{-1} \mathbf{h}$

Gershgorin & Shavitt, IJQC 2 (1968) 751



$$Hc - Ec = \begin{pmatrix} H^{(0)} & h^\dagger & 0 \\ h & H^{(1)} & g^\dagger \\ 0 & g & H^{(2)} \end{pmatrix} \begin{pmatrix} c^{(0)} \\ c^{(1)} \\ c^{(2)} \end{pmatrix} - E \begin{pmatrix} c^{(0)} \\ c^{(1)} \\ c^{(2)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

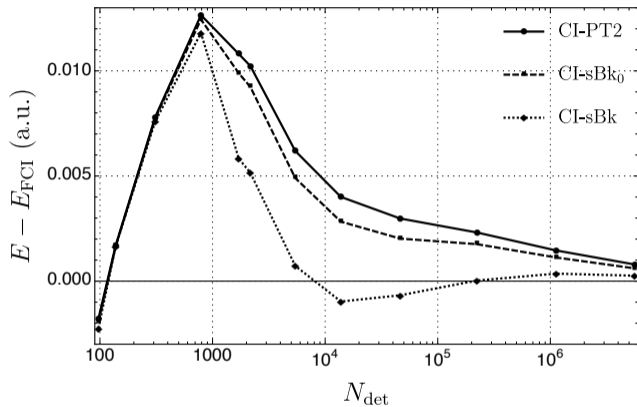
internal space $ I\rangle$	$H^{(0)}$	h^\dagger	0	external space
	h	$H^{(1)}$	g^\dagger	
perturbers $ \alpha\rangle$	0	g	$H^{(2)}$	
FCI space				

$$\Rightarrow c^{(1)} = - \left[(H^{(1)} - EI) - g^\dagger (H^{(2)} - EI) g \right]^{-1} h c^{(0)}$$

Effective Hamiltonian: $H_{\text{eff}} = H^{(0)} + \Delta$ Dressing term: $\Delta = h^\dagger c^{(1)}$

Approximation #2 (shifted-Bk method): $\Delta = h^\dagger (E^{(0)} - D^{(1)})^{-1} h$

Davidson, McMurchie & Day, IJQC 74 (1981) 5491



Scemama, Garniron, Giner, Caffarel & Loos, JCP 149 (2018) 064103

- ▶ Multi-state version also available
- ▶ Provides better trial wave functions for QMC



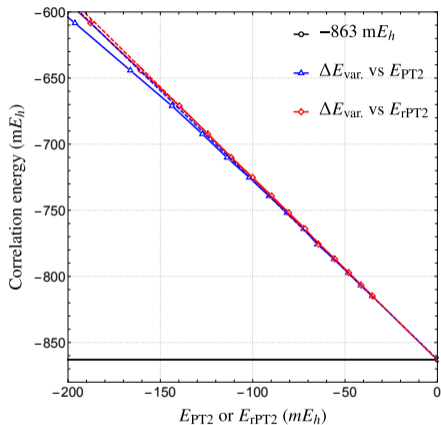
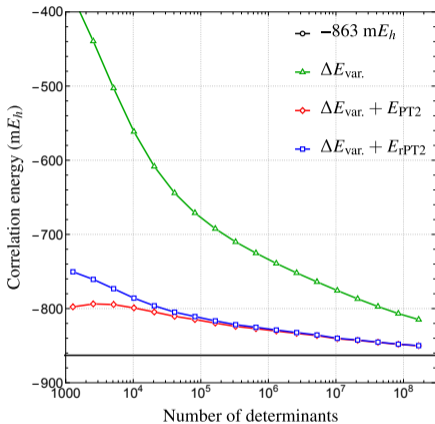
The Benzene Blind Challenge: Frozen-core correlation energy (cc-pVDZ)

The Benzene Blind Challenge

ASCI
SHCI
iCI
AS-FCIQMC
CAD-FCIQMC
DMRG
MBE-FCI
FCCR



Eriksen et al. JPCL 11 (2020) 8922



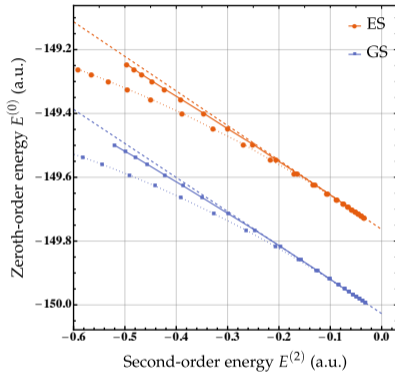
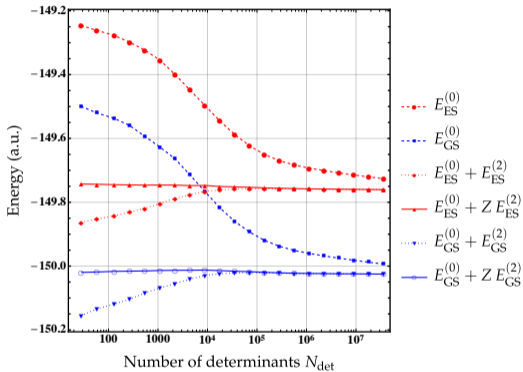
Loos, Damour & Scemama JCP 153 (2020) 176101

TABLE I. The frozen-core correlation energy ΔE (in mE_h) of benzene in the $cc\text{-pVDZ}$ basis set using various methods.

Method	ΔE	Ref.
ASCI	-860.0	17
iCI	-861.1	17
CCSDTQ	-862.4	17
DMRG	-862.8	17
FCCR	-863.0	17
MBE-FCI	-863.0	17
CAD-FCIQMC	-863.4	17
AS-FCIQMC	-863.7	17
SHCI	-864.2	17
ph-AFQMC	-864.3(4)	45
CIPSI	-863.4	This work

TABLE III. Extrapolation distances, ΔE_{dist} , defined as the difference between the final computed energy, ΔE_{final} , and the extrapolated energy, ΔE_{extrap} , associated with ASCI, iCI, SHCI, DMRG, and CIPSI for the best blind-test and post-blind-test estimates of the correlation energy of benzene in the $cc\text{-pVDZ}$ basis. The final variational energies ΔE_{var} are also reported. See Ref. 17 for more details. All correlation energies are given in mE_h .

Method	ΔE_{var}	ΔE_{final}	ΔE_{extrap}	ΔE_{dist}
Best blind-test estimates				
ASCI	-737.1	-835.4	-860.0	-24.6
iCI	-730.0	-833.7	-861.1	-27.4
SHCI	-827.2	-852.8	-864.2	-11.4
DMRG	-859.2	-859.2	-862.8	-3.6
Best post-blind-test estimates				
ASCI	-772.4	-835.2	-861.3	-26.1
iCI	-770.7	-842.8	-864.2	-21.3
SHCI	-835.2	-854.9	-863.6	-8.7
CIPSI	-814.8	-850.2	-863.4	-13.2



Garniron et al., JCTC 15 (2019) 3591



Table 1. Zeroth-Order Energy $E^{(0)}$, Second-Order Perturbative Correction $E^{(2)}$, and Its Renormalized Version $\text{ZE}^{(2)}$ (in hartree) of CN3 for Increasingly Large Wave Functions^a

N_{det}	$E^{(0)}$		$E^{(0)} + E^{(2)}$			$E^{(0)} + \text{ZE}^{(2)}$		
	GS (a.u.)	ES (a.u.)	GS (a.u.)	ES (a.u.)	$\Delta E(\text{eV})$	GS (a.u.)	ES (a.u.)	$\Delta E(\text{eV})$
28	-149.499574	-149.246268	-150.155(1)	-149.863(1)	7.95(5)	-150.020(1)	-149.743(1)	7.54(5)
58	-149.519908	-149.261390	-150.134(1)	-149.853(1)	7.67(5)	-150.018(1)	-149.744(1)	7.48(5)
131	-149.537424	-149.277496	-150.118(1)	-149.8427(9)	7.52(4)	-150.017(1)	-149.7449(9)	7.39(4)
268	-149.559465	-149.298484	-150.1035(9)	-149.8308(9)	7.42(4)	-150.0158(9)	-149.7457(9)	7.35(4)
541	-149.593434	-149.323302	-150.0845(8)	-149.8186(8)	7.24(4)	-150.0152(8)	-149.7463(8)	7.32(4)
1101	-149.627202	-149.354807	-150.0683(8)	-149.8045(8)	7.18(3)	-150.0137(8)	-149.7460(8)	7.28(3)
2207	-149.663850	-149.399522	-150.0549(7)	-149.7879(7)	7.26(3)	-150.0132(7)	-149.7462(7)	7.27(3)
4417	-149.714222	-149.448133	-150.0409(6)	-149.7762(6)	7.20(3)	-150.0130(6)	-149.7478(6)	7.22(3)
8838	-149.765886	-149.496401	-150.0296(5)	-149.7655(5)	7.19(2)	-150.0124(5)	-149.7473(5)	7.21(2)
17 680	-149.817301	-149.545048	-150.0239(4)	-149.7615(4)	7.14(2)	-150.0141(4)	-149.7505(4)	7.17(2)
35 380	-149.859737	-149.587668	-150.0216(3)	-149.7582(3)	7.17(1)	-150.0161(3)	-149.7518(3)	7.19(1)
70 764	-149.893273	-149.623235	-150.0207(2)	-149.7566(3)	7.18(1)	-150.0174(2)	-149.7530(3)	7.19(1)
141 545	-149.919463	-149.650109	-150.0214(2)	-149.7572(2)	7.189(8)	-150.0194(2)	-149.7550(2)	7.196(8)
283 108	-149.937839	-149.669735	-150.0224(2)	-149.7576(2)	7.206(7)	-150.0211(2)	-149.7562(2)	7.209(7)
566 226	-149.950918	-149.683278	-150.0233(1)	-149.7580(1)	7.217(6)	-150.0223(1)	-149.7570(1)	7.219(6)
1 132 520	-149.960276	-149.693053	-150.0238(1)	-149.7588(1)	7.212(5)	-150.0231(1)	-149.7580(1)	7.214(5)
2 264 948	-149.968203	-149.700907	-150.0240(1)	-149.7590(1)	7.211(4)	-150.0235(1)	-149.7584(1)	7.212(4)
4 529 574	-149.975230	-149.708061	-150.0245(1)	-149.7594(1)	7.215(4)	-150.0241(1)	-149.7589(1)	7.216(4)
9 057 914	-149.981770	-149.714526	-150.02463(9)	-149.75981(8)	7.206(3)	-150.02434(9)	-149.75948(8)	7.207(3)
18 110 742	-149.987928	-149.720648	-150.02495(7)	-149.76025(8)	7.203(3)	-150.02474(7)	-149.76000(8)	7.204(3)
36 146 730	-149.993593	-149.726253	-150.02527(6)	-149.76065(7)	7.198(3)	-150.02502(6)	-149.760 47(7)	7.198(3)

^aThe excitation energy ΔE (in eV) is the energy difference between the ground state (GS) and the excited state (ES). The statistical error, corresponding to one standard deviation, is reported in parentheses.



✗ Forget about large systems/basis sets:

JCTC 16 (2020) 1711

- ▶ 1-3 non-H atoms with triple- (30-44) or quadruple- ζ basis (55-80)
- ▶ 4-6 non-H atoms with double- ζ basis (14-23)

✓ Open-shell systems are “easy” (no spin contamination and independent of starting orbitals)

JCTC 16 (2020) 3720

✓ Double excitations are easily accessible (especially if they have the same symmetry as the ground state)

JCTC 15 (2020) 1939

✓ You can post-process CIPSI wave functions!