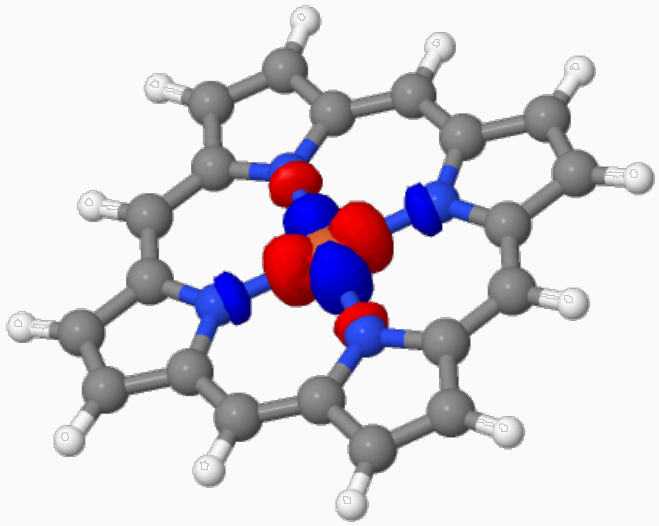
Cheap and Near Exact CASSCF with Large Active Spaces

James E. T. Smith

University of Colorado, Boulder, Department of Chemistry



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Background

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Solve for orbital rotation param. $\hat{\kappa}$.

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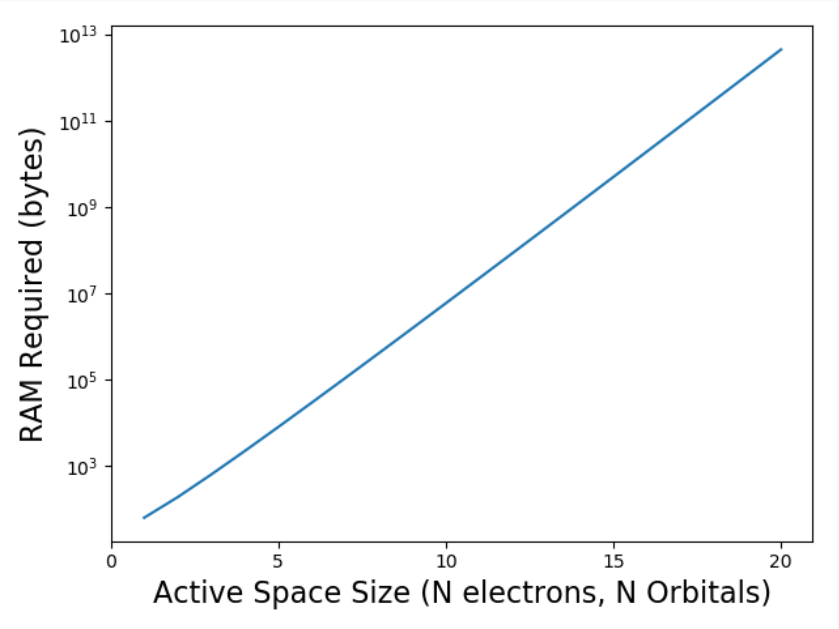
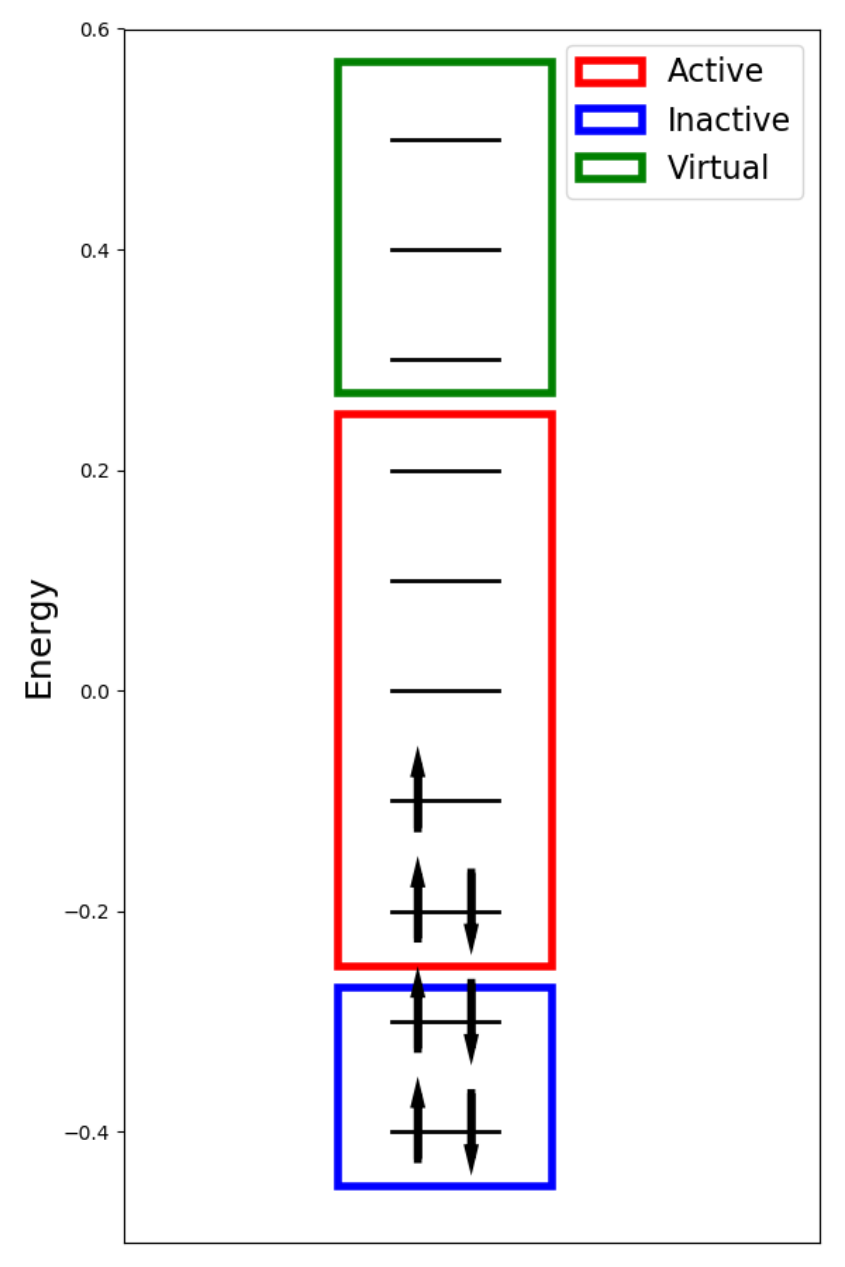
- E.g. (20e,20o) $\rightarrow$ 4.4 TB!



Complete Active Space CI (CASCI)

- Partition orbitals into inactive, active, and virtual



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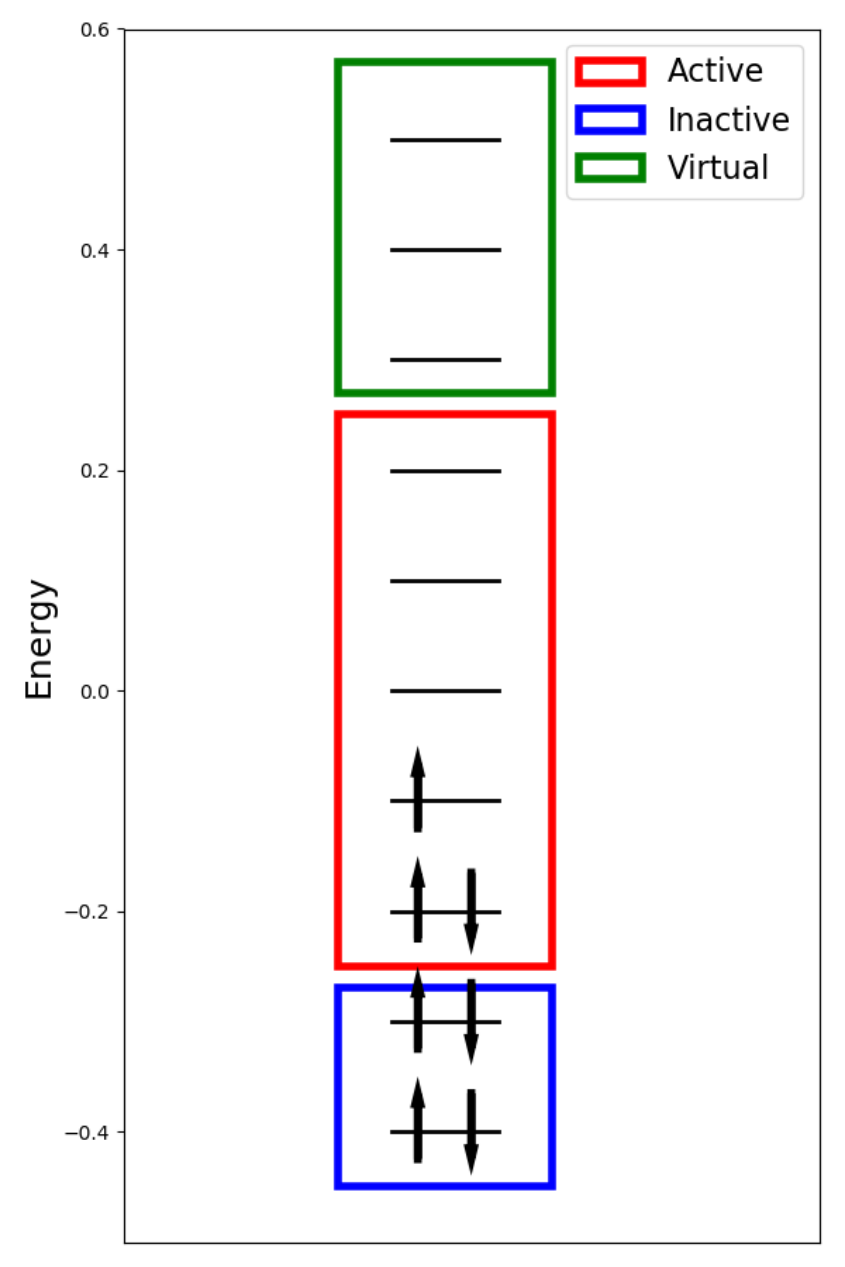

Complete Active Space CI (CASCI)

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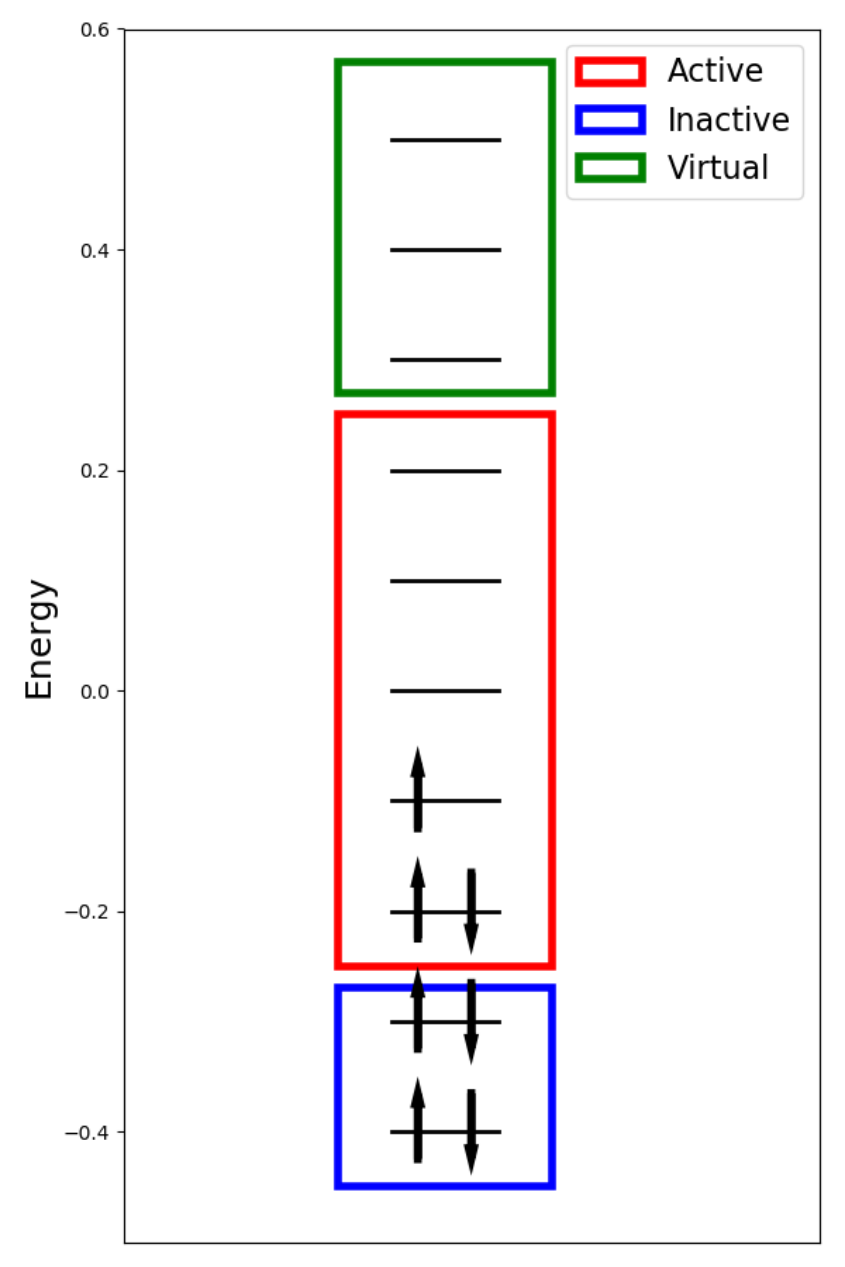
- FCI procedure for a subset of orbitals and electrons
- Scales combinatorially with active space size



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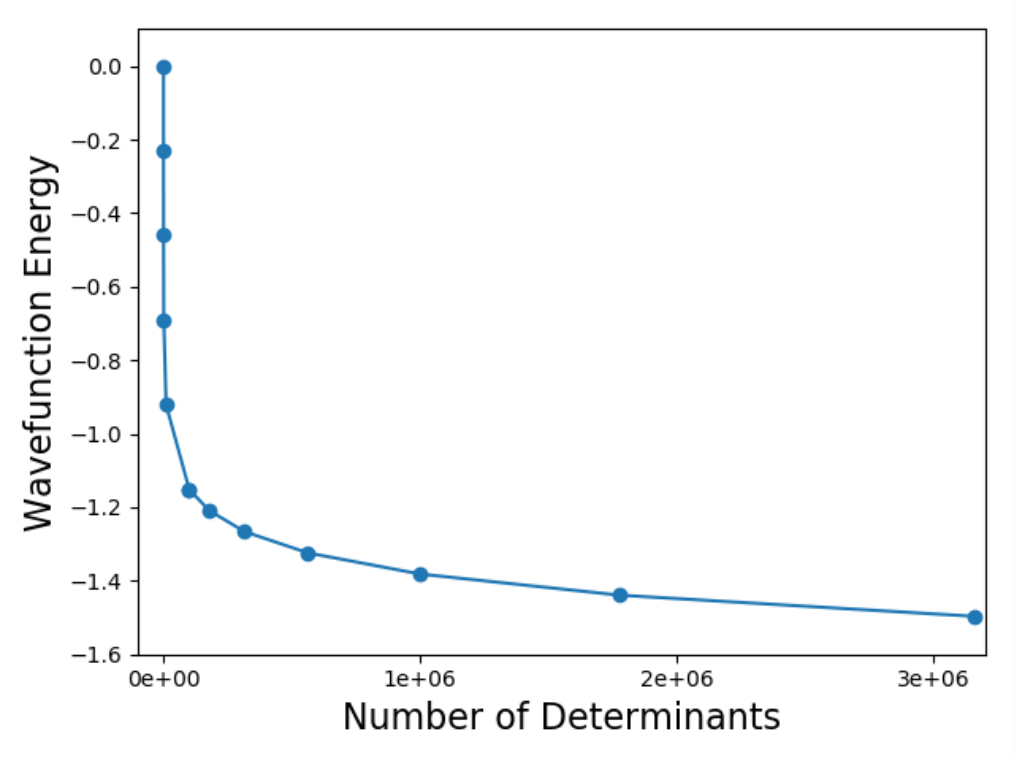

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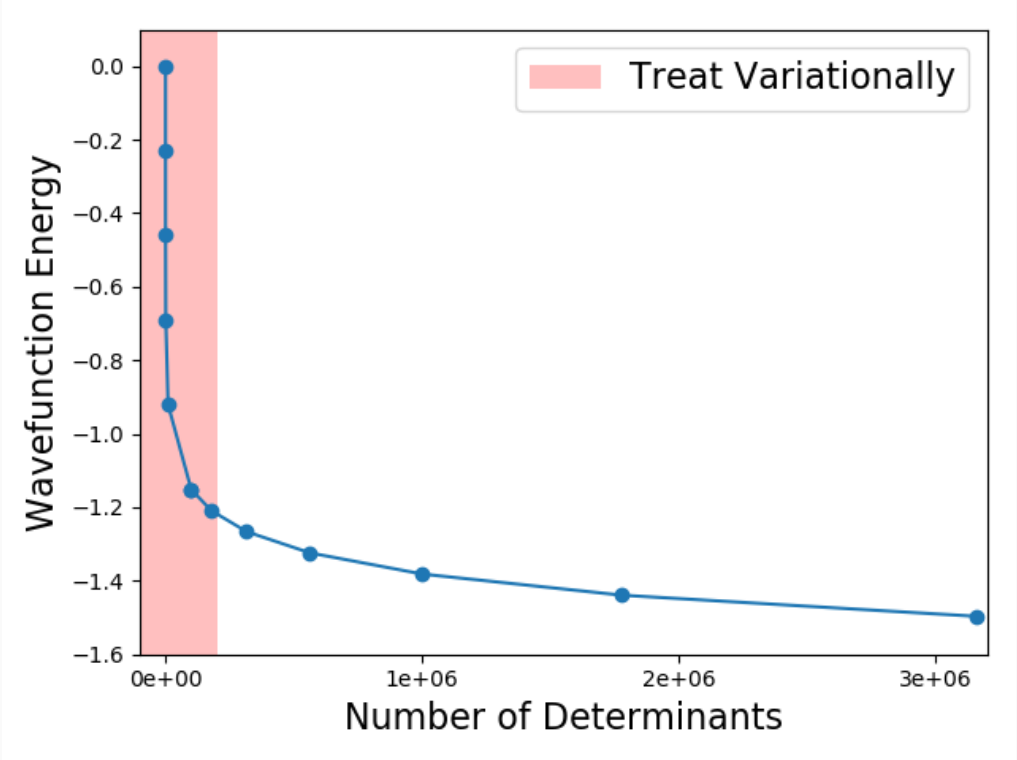

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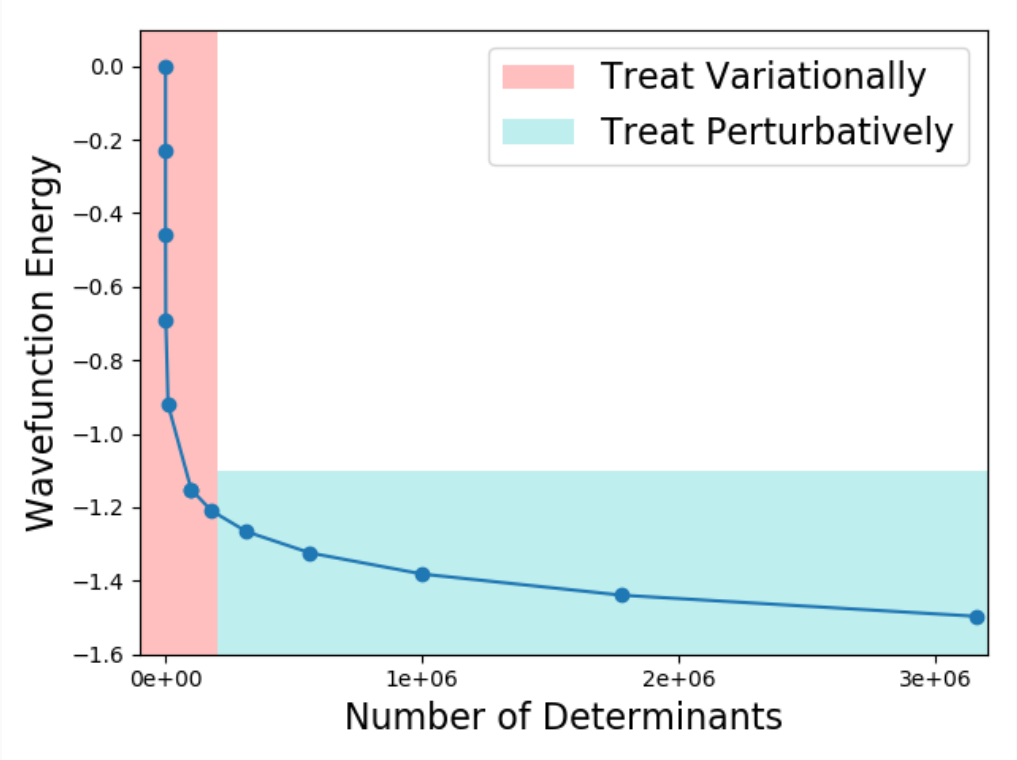
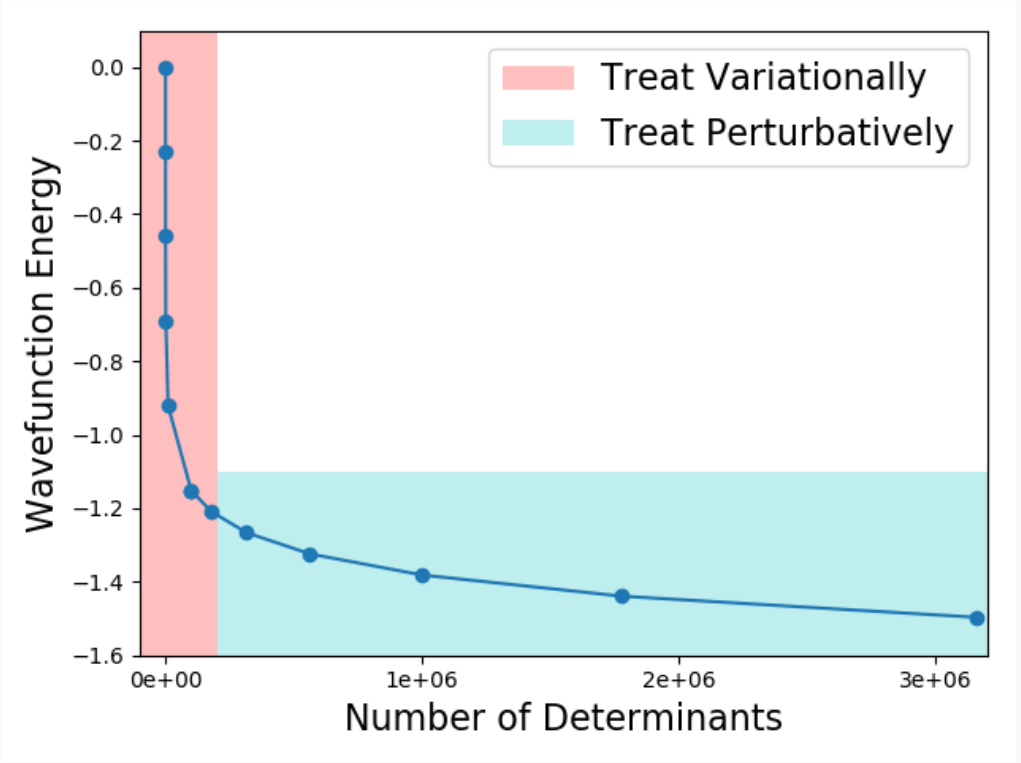


Selected CI

- Many of the determinants in CAS wavefunctions are not important
- Treat important determinants variationally
- Treat remaining determinants perturbatively
- How do we *select* the "important" determinants?



CIPSI vs. HCI

$$f^{\mu}_{\mathrm{CIPSI}}(|D_a\rangle) = \left| \frac{\sum_{|D_i\rangle \in \mathcal{V}^{\mu}} H_{ai} c_i^{\mu}}{E_0 - E_a} \right| \quad (3)$$

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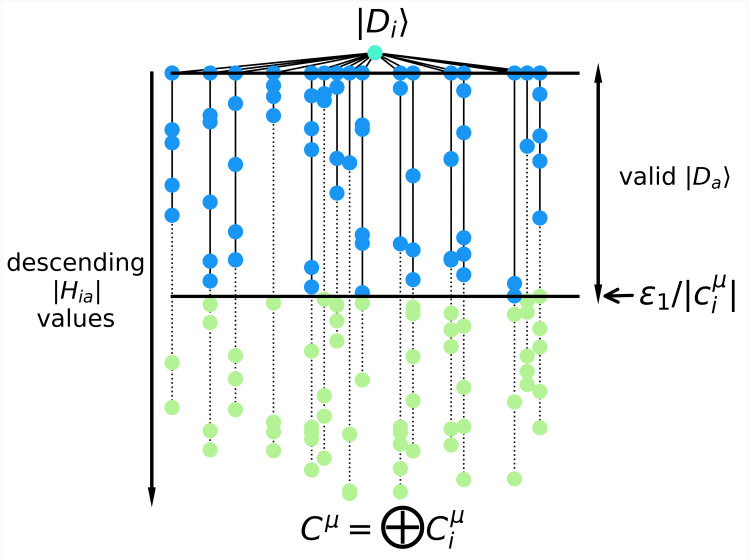

HCI Algorithm: Variational Stage

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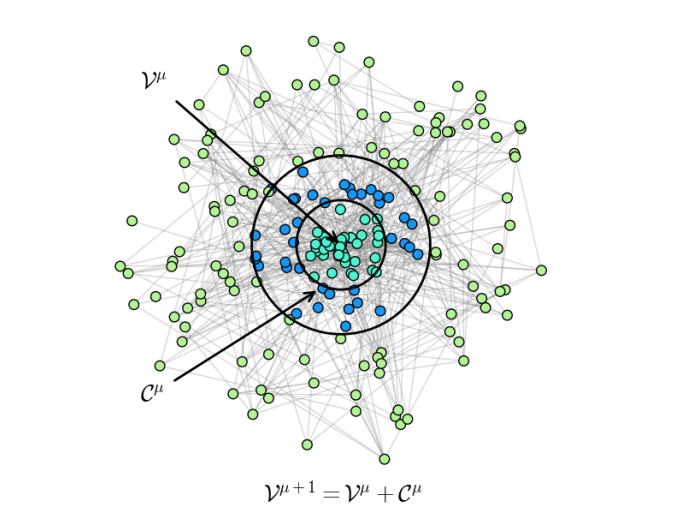
Wavefunction at iteration μ:

$$|\Psi_0^\mu\rangle = \sum_{|D_i\rangle \in \mathcal{V}^\mu} c_i^\mu \, |D_i\rangle \qquad (5)$$



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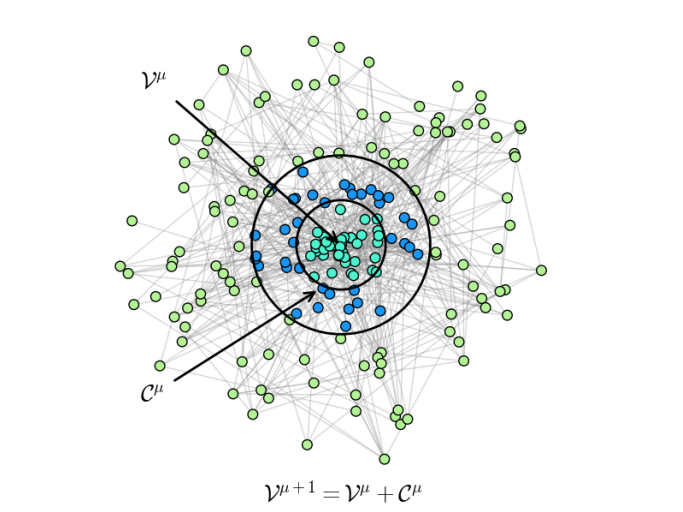

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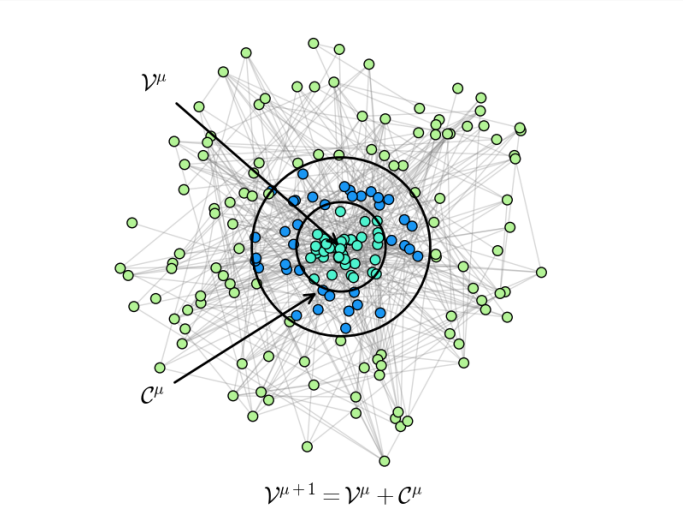
Importance Criterion (add to $\mathcal{V}^\mu$?):

$$f^\mu_{\mathrm{HCI}}(|D_a\rangle) = \max_{|D_i\rangle \in \mathcal{V}^\mu} |H_{ai} c_i^\mu| \qquad (7)$$



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HCI Algorithm: Perturbative Stage

Epstein-Nesbet Hamiltonian:

$$\hat{H}_0 = \sum_{|D_i\rangle, |D_j\rangle \in \mathcal{V}} H_{ij} \left|D_i\right\rangle \left\langle D_j\right| + \sum_{|D_a\rangle \notin \mathcal{V}} H_{aa} \left|D_a\right\rangle \left\langle D_a\right| \tag{8}$$

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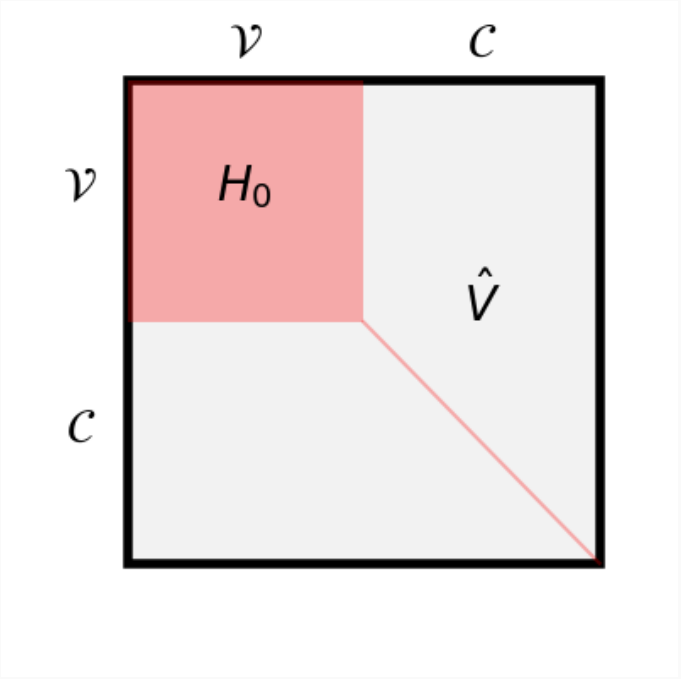

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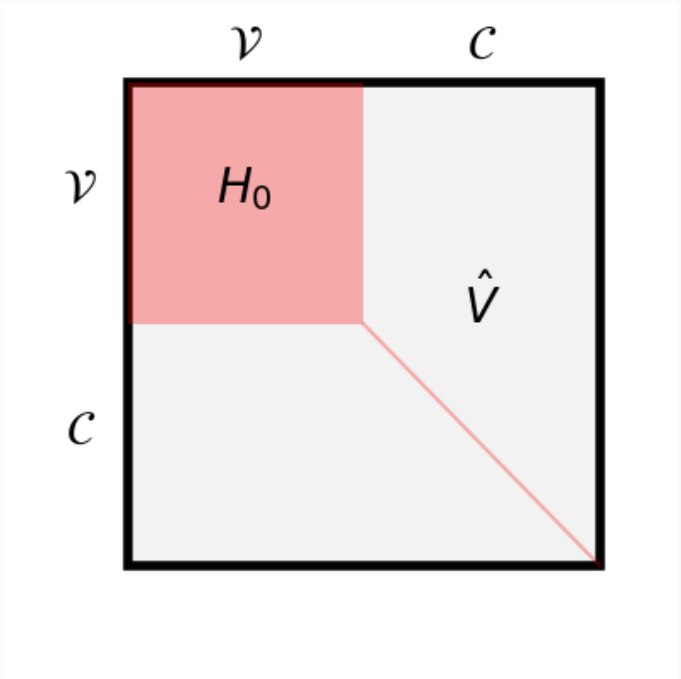

Deterministic perturbative energy correction using subset of determinants (determined by ϵ_2):

$$E_2(\epsilon_2) = \sum_{|D_a\rangle \in \mathcal{C}(\epsilon_2)} \frac{1}{E_0 - H_{aa}} \left(\sum_{|D_i\rangle \in \mathcal{V}}^{(\epsilon_2)} H_{ai} c_i \right)^2 \tag{9}$$

Semistochastic HCI (SHCI)

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Reduce stochastic noise by calculating tractable part of PT correction deterministically

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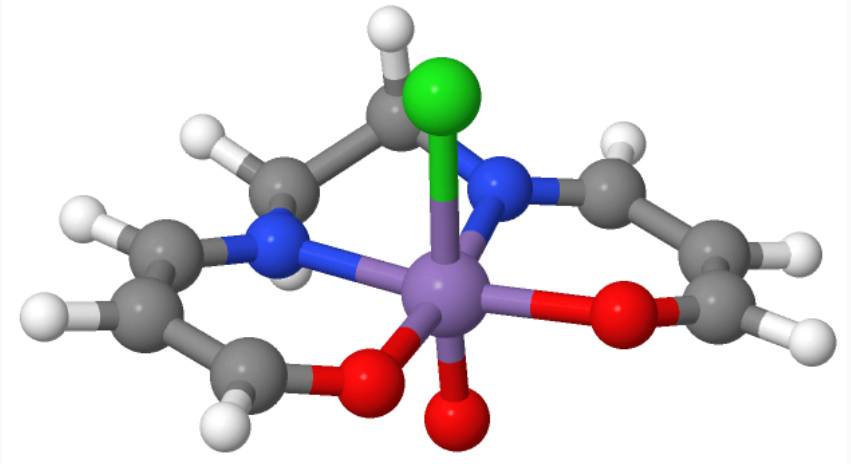
Routine active space of (28e, 22o)



Mn(salen)

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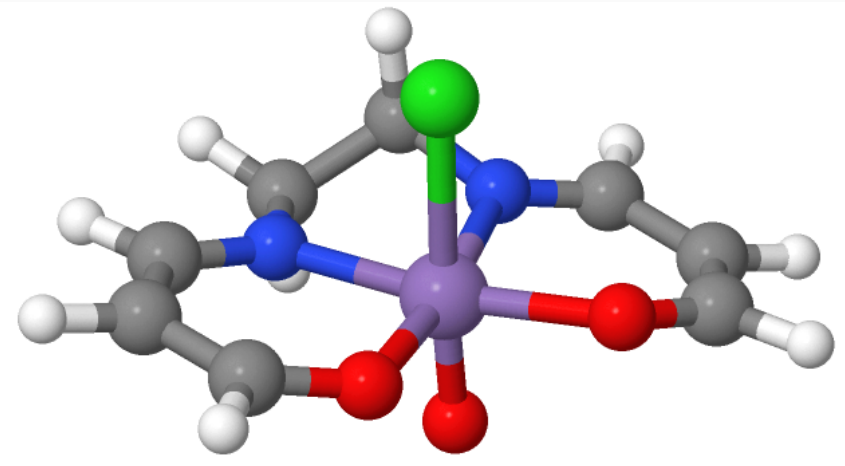
Routine active space of (28e, 22o)

Sym.	N_{var}	SHCI (Ha)	DMRG (Ha)	Time (sec)
^1A	232484	0.7980(7)	0.7991	37
^3A	208334	0.7994(8)	0.8001	32

Table 1: All energies shifted by 2251 Ha.



Mn(salen)

Butadiene

Large active space (22e, 82o)

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ϵ_1	N_{var}	vHCI	SHCI
3×10^{-5}	1.1×10^7	-0.5411	-0.5534(1)
2×10^{-5}	2.1×10^7	-0.5441	-0.5540(1)
1×10^{-5}	5.9×10^7	-0.5481	-0.5550(1)
	CCSD(T)	-0.5550	
	CCSDT	-0.5560	
	DMRG(M=6000)	-0.5572	

Table 2: All energies shifted by 155 Ha.

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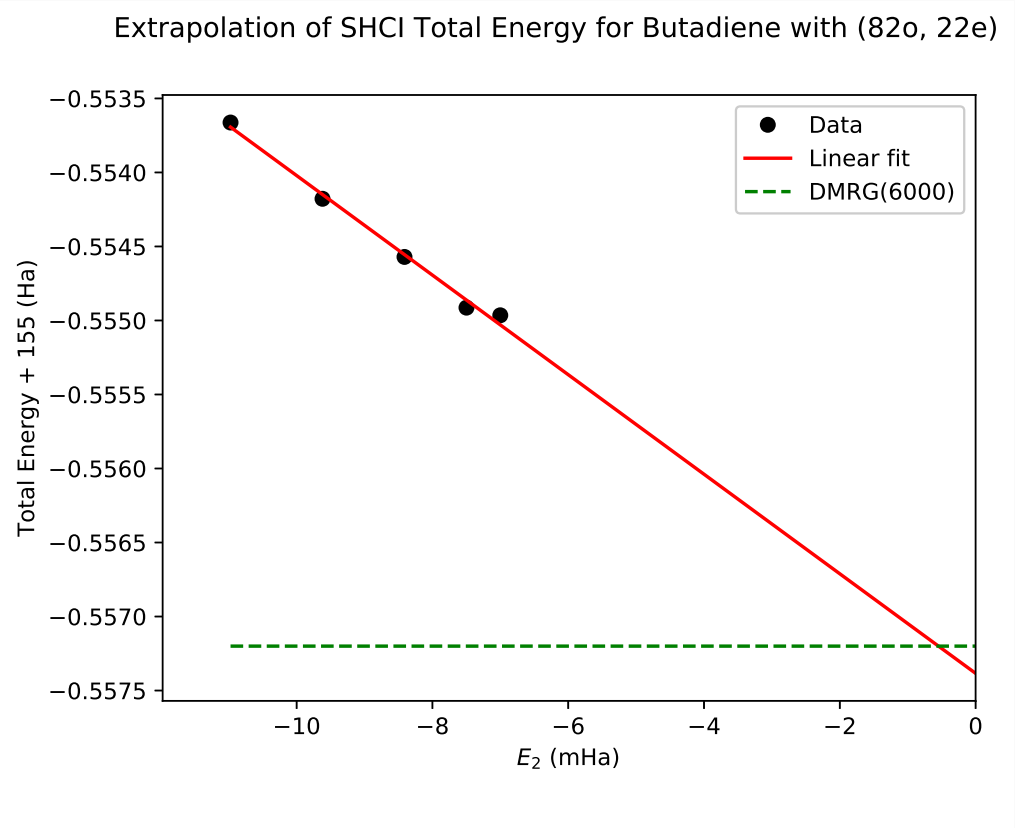

Figure 2: Smith et al. 2017.

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Multiconfigurational Self Consistent Field (MCSCF) wavefunction:
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Solve for C_i and $\hat{\kappa}$.

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Objective: Use SHCI instead of CASCI to solve for C_i coefficients in CASSCF-like calculations.

Connecting to PySCF: Overview

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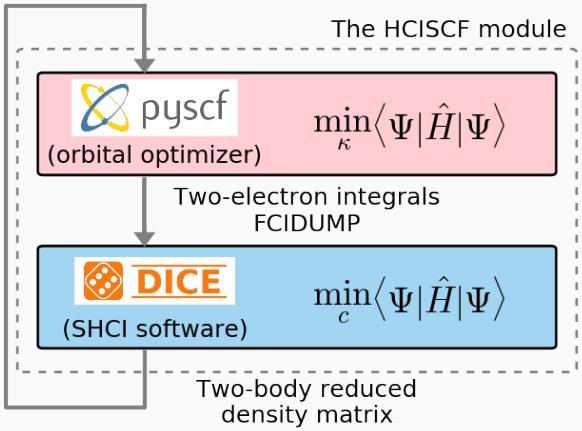
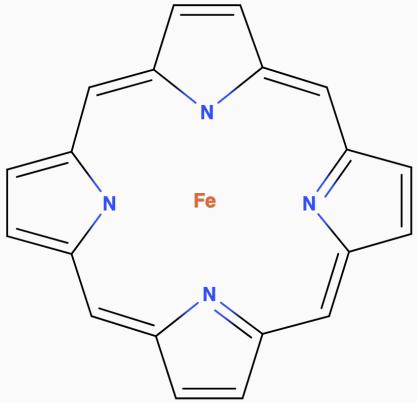


Figure 3: Overview of workflow for HCISCF module from Smith et al. 2017

HCISCF: Converging the Multiconfigurational Orbitals

- PT does not improve convergence of orbitals



	ϵ_1 (Ha)	E_{HCISCF} (Ha)	E_{SHCI} (Ha)
HCISCF	5×10^{-5}	-2245.0178	-2245.0314
vHCISCF	5×10^{-5}	-2245.0121	-2245.0313

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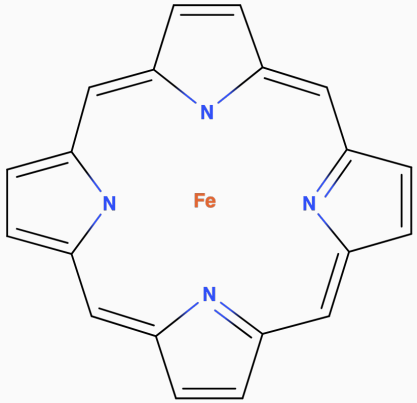
- "Loose" ϵ_1 values converge orbitals



	ϵ_1 (Ha)	E_{HCISCF} (Ha)	E_{SHCI} (Ha)
HCISCF	5×10^{-5}	-2245.0178	-2245.0314
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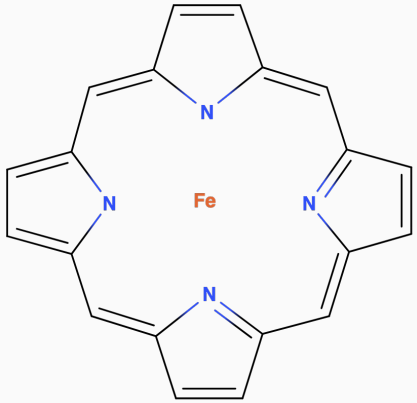

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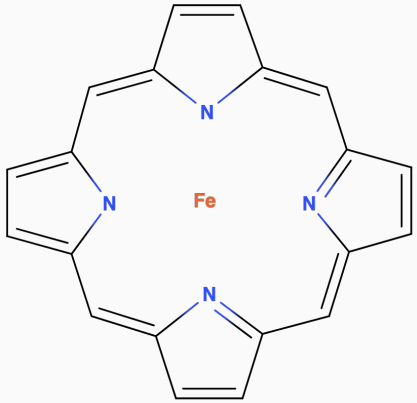

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Workflow

1. Run HCISCF with only variational HCI and "loose" ϵ_1 (fewer determinants) to generate multiconfigurational orbitals
2. Run final SHCI calculation w/ tight settings to get final energy

Speed of HCISCF

- Optimization of CI coefficients is **not** bottleneck even for large active spaces

Total Orbitals	CAS	T_{OO} (sec)	T_{CI} (sec)
439	(29o, 32e)	126	52
956	(29o, 32e)	2236	70

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Total Orbitals	CAS	T_{OO} (sec)	T_{CI} (sec)
439	(29o, 32e)	126	52
439	(44e, 44o)	264	147
956	(29o, 32e)	2236	70

Applications

Fe(porphyrin): Motivation

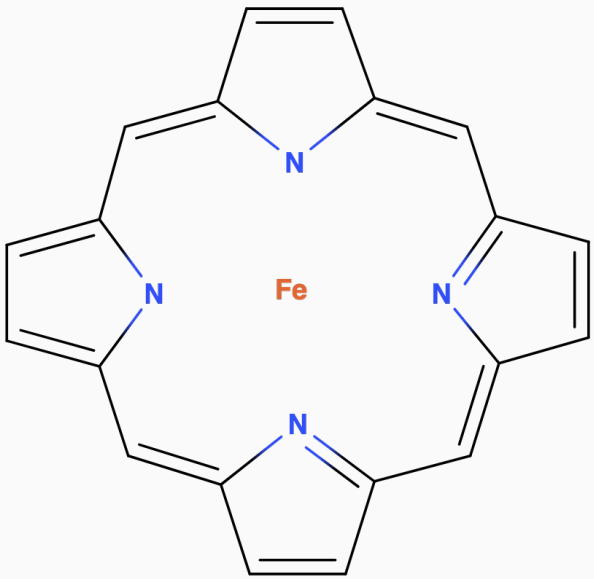
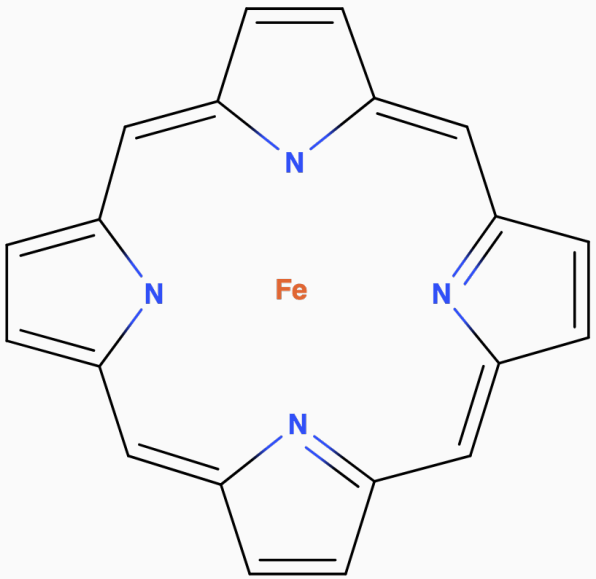


Figure 4: Fe(II)(porphyrin)

- Model system for active site of heme group

Fe(porphyrin): Motivation



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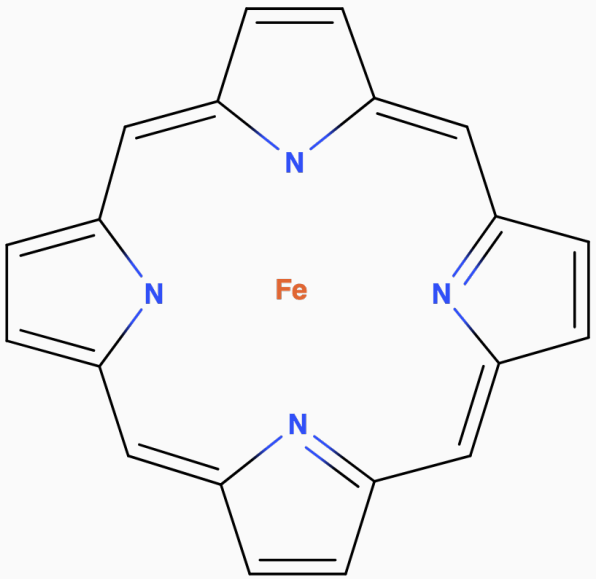

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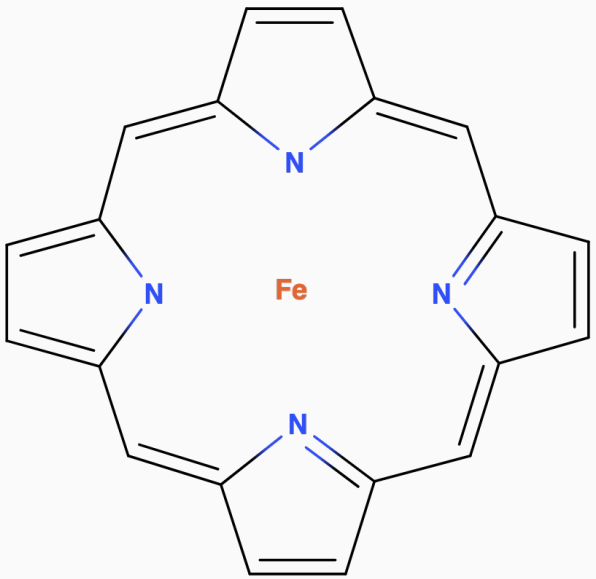

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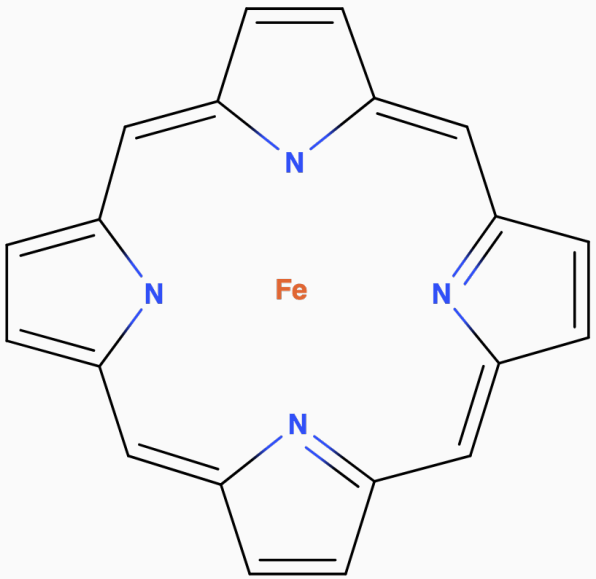

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- Almost all theoretical work suggests ${}^5A_{1g}$

Fe(porphyrin): CAS(32e,29o)

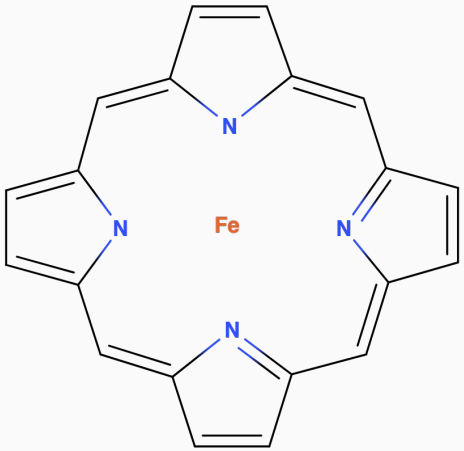

Figure 5: Fe(II)(porphyrin)

- Fe 3d and all the conjugated π orbitals in active space

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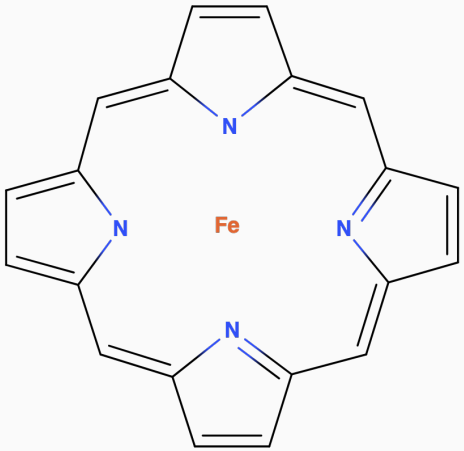

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Basis	Sym.	E_{SHCI} (Ha)	E_{ex} (kcal/mol)
CAS(29o, 32e)			
cc-pVDZ	^5A_g	-2245.0314(5)	16.7
cc-pVDZ	$^3B_{1g}$	-2245.0049(6)	
cc-pVTZ	^5A_g	-2245.2549(5)	16.4
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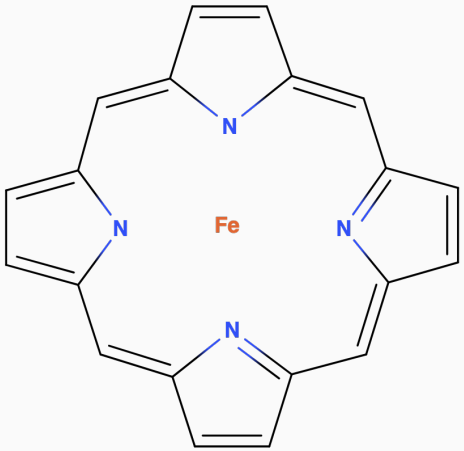

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- Add Fe-N 2px/y and stabilize triplet by adding Fe 4d

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cc-pVTZ	$^3B_{1g}$	-2245.2288(6)	
	CAS(44o,44e)		
cc-pVDZ	^5A_g	-2245.1964(9)	**-2.0**
cc-pVDZ	$^3B_{1g}$	-2245.1995(6)	

Fe(porphyrin): Wrap up

- Only takes a few hours to run (44e,44o) calculation!
- Suggest that previous work disagreed because of choice of active space, i.e. need to include Fe-N bonding/anti-bonding and second d shell

Capturing Dynamical Correlation

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  - Total density and pair density
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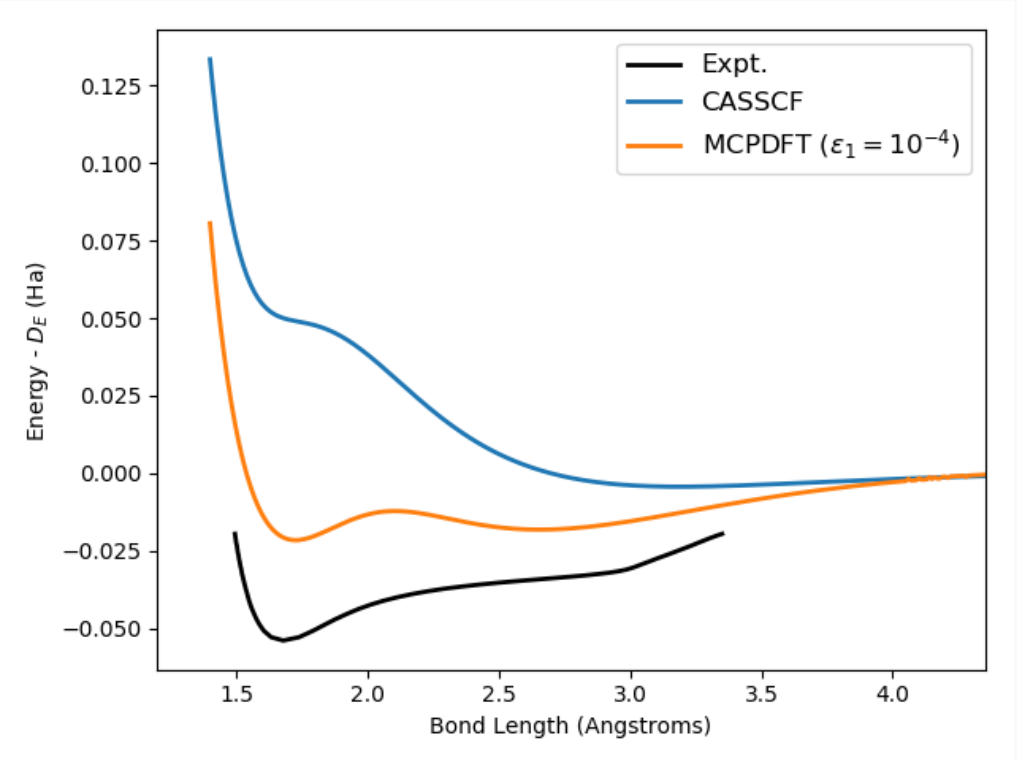
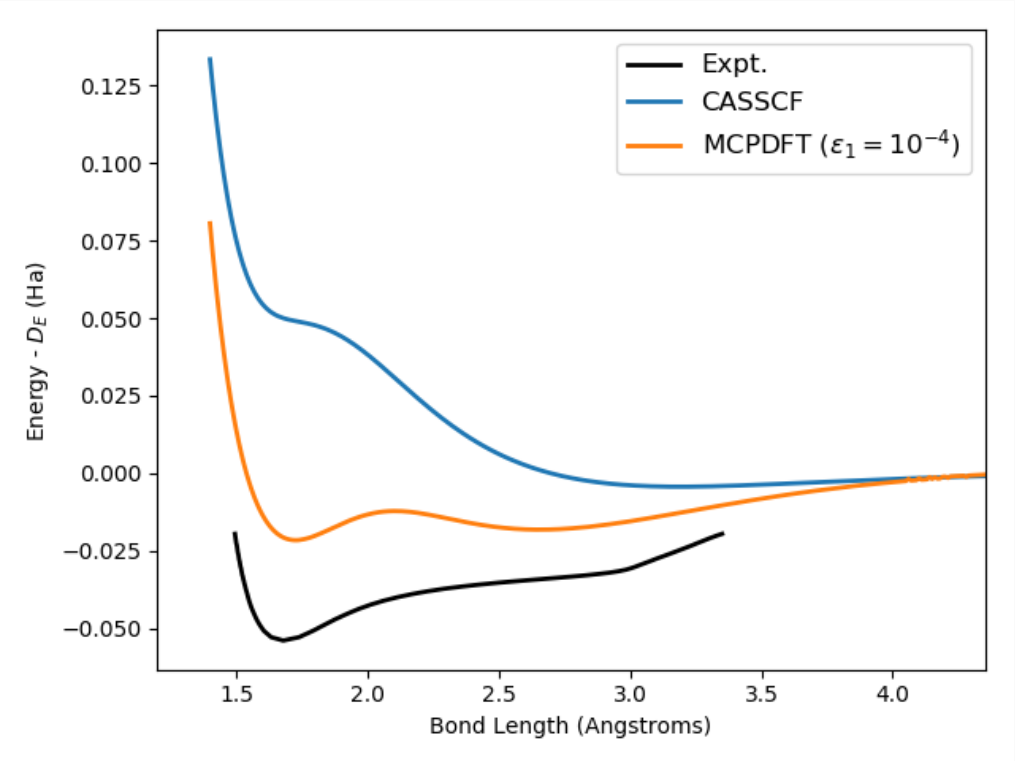


MC-PDFT

Cr_2 CAS(12e, 12o)

- CASSCF wavefunctions do not produce bound dissociation curve
- MC-PDFT with HCISCF reference wavefunctions produce bound curves
- Good agreement with MC-PDFT using CASSCF wavefunctions (G. L. Manni and Gagliardi 2014)



Conclusions and Future Work

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- Performed CASSCF-like calculation with (44e, 44o) in only a few hours

Up next:

- Using MC-PDFT with large active space reference wavefunctions
- Calculating nuclear gradients of SHCI energy

Acknowledgements

Thanks to the Sharma Group at CU Boulder and particular: Sandeep Sharma, Bastien Mussard, and Adam Holmes for helpful discussion and offering countless advice. This work was supported by

- University of Colorado Boulder startup grant
- The GAANN Fellowship
- MolSSI Phase I Software Fellowship

And thank you Qiming!

Questions

Thanks you for your attention!
Do you have any questions?

https://sanshar.github.io/Dice/

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