

A New, Cheap, and Accurate CASSCF-like Method

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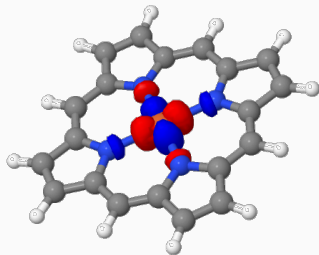


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Background

Working in Second Quantization

- Working with occupation number vectors (determinants) i.e.
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$$|\Psi\rangle = \sum_i C_i |i\rangle \quad (1)$$

Single Reference Methods

HF wavefunction:

$$|\kappa\rangle = \exp(-\hat{\kappa}) |0\rangle \quad (2)$$

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

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CI wavefunction

$$|\mathbf{C}\rangle = \sum_i C_i |i\rangle \quad (4)$$

Solve for determinant coefficient C_i .

FCI wavefunction:

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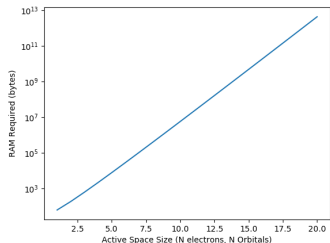


Figure 1: Log plot of RAM required for storing FCI determinants.

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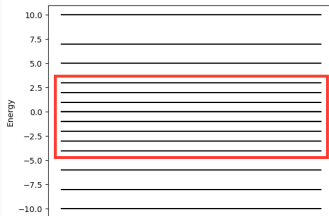


Figure 2: General MO diagram showing partitioning of the active space. Highlighted orbitals around fermi level are active, above and below are the virtual and inactive respectively.

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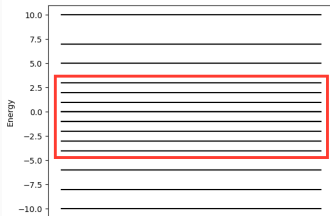


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- Still scales combinatorially, this time with size of the active space

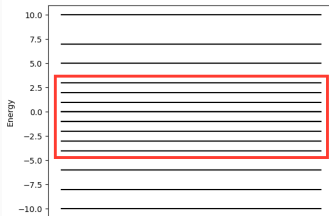


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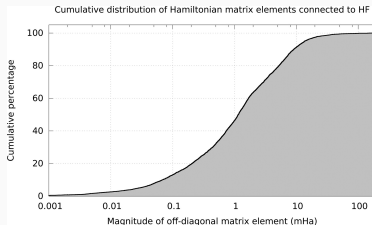


Figure 3: Hamiltonian elements connected determinants to HF span many orders of magnitude, so there are lots of unimportant determinants that do not significantly impact our WF. From Holmes, Tubman, and Umrigar 2016

Working smarter, not harder

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- Select determinants for variational space more intelligently
- HCI approximates FCI w/in the active space through variational WF optimization and a perturbative energy correction

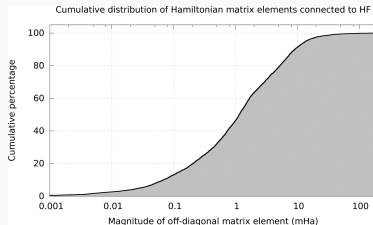


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HCI Algorithm: Variational Stage

Goal: iteratively grow
variational determinant space where our
WF lives

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Wavefunction at iteration μ :

$$|\Psi_0^\mu\rangle = \sum_{|D_i\rangle \in \mathcal{V}^\mu} c_i^\mu |D_i\rangle \quad (6)$$

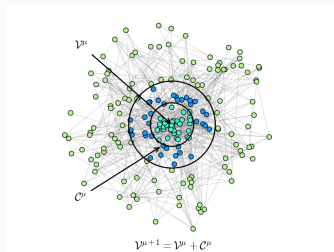


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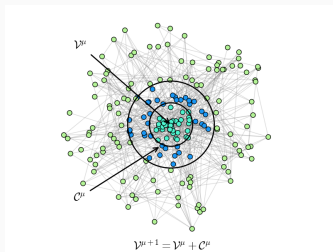


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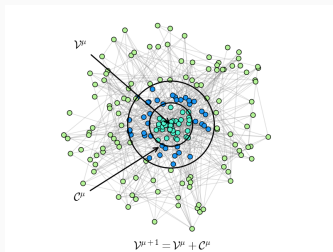


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Only requires single parameter ϵ_1

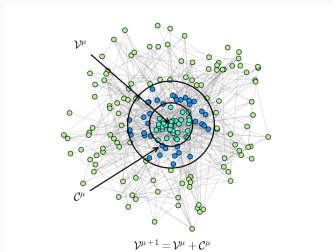


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HCI Algorithm: Perturbative Stage

Epstein-Nesbet PT Hamiltonian:

$$\hat{H}_0 = \sum_{|D_i\rangle, |D_j\rangle \in \mathcal{V}} H_{ij} |D_i\rangle \langle D_j| + \sum_{|D_a\rangle \notin \mathcal{V}} H_{aa} |D_a\rangle \langle D_a| \quad (9)$$

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

$$E_2(\epsilon_2) = \sum_{|D_a\rangle \in \mathcal{C}(\epsilon_2)} \frac{1}{E_0 - H_{aa}} \left(\sum_{|D_i\rangle \in \mathcal{V}}^{(\epsilon_2)} H_{ai} c_i \right)^2 \quad (10)$$

$$E_2 = \langle \Psi_0 | \hat{V} \frac{1}{E_0 - \hat{H}_0} \hat{V} | \Psi_0 \rangle \quad (11)$$

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Reduce stochastic noise by calculating tractable part of PT correction deterministically

$$E_2(\epsilon_2) = E_2^D(\epsilon_2^d) + (E_2^S(\epsilon_2) - E_2^S(\epsilon_2^d)) \quad (12)$$





Table 1: All energies shifted by 155 Ha.

ϵ_1	N_{var}	vHCl	SHCl
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		
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DMRG(M=6000)	-0.5572		



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SHCI($\epsilon_1 \rightarrow 0$)		-0.5574(8)	
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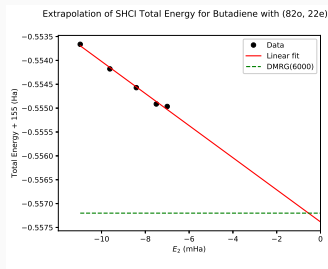


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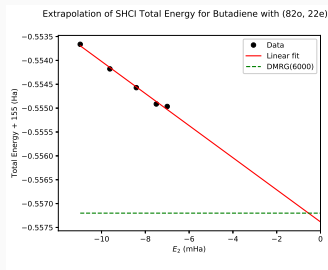


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- **W/in chemical accuracy even before extrapolation**
- We can set ϵ_2 arbitrarily low so we effectively have a single parameter ϵ_1

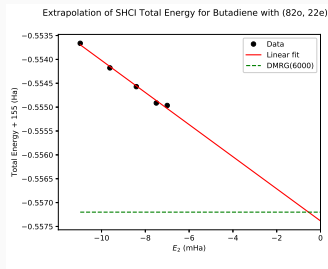


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HCISCF

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Multiconfigurational Self Consistent Field (MCSCF) wavefunction:

$$|\kappa, \mathbf{C}\rangle = \exp(-\hat{\kappa}) \sum_i C_i |i\rangle \quad (14)$$

Solve for C_i and $\hat{\kappa}$.

Using only variational (vHCISCF)

Energy of variational portion of HCl:

$$E_{HCl}[\boldsymbol{\kappa}, \mathbf{c}] = E_0[\boldsymbol{\kappa}, \mathbf{c}] \quad (15)$$

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Energy gradient w.r.t orbital rotation parameter

$$\frac{dE_{HCl}}{d\boldsymbol{\kappa}} = \frac{\partial E_0}{\partial \boldsymbol{\kappa}} + \frac{\partial E_0}{\partial \mathbf{c}} \frac{d\mathbf{c}}{d\boldsymbol{\kappa}} = \frac{\partial E_0}{\partial \boldsymbol{\kappa}} \quad (16)$$

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$$= \sum_{ijkl} \frac{\partial H_{0,ijkl}}{\partial \boldsymbol{\kappa}} \Gamma_{ijkl}^{\mathbf{c}, \mathbf{c}} \quad (17)$$

Energy as a function of orb. rot. param. κ , Lagrangian multiplier \mathcal{E}_0 , and the determinant coefficients in the variational (**c**) and perturbative (**d**) wavefunctions.

$$E_{\text{HCl}}[\kappa, \mathbf{c}, \mathcal{E}_0, \mathbf{d}] = E_0[\kappa, \mathbf{c}, \mathcal{E}_0] + E_2[\kappa, \mathbf{c}, \mathbf{d}] \quad (18)$$

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Energy gradient w.r.t. orbital rotation parameter κ :

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Derivatives of CI coefficients w.r.t. κ are messy to calculate. We want Eq. 19 to be stationary w.r.t. all parameters.

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Generally we have $E[\mathbf{V}, \mathbf{T}]$, where \mathbf{V} are variational parameters and \mathbf{T} are non-variational ones ($w/ \frac{\partial E}{\partial \mathbf{V}} = 0$ and the general rule $R[\mathbf{T}] = 0$)

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Create the following Lagrangian:

$$L[\mathbf{V}, \mathbf{T}, \lambda] = E[\mathbf{V}, \mathbf{T}] + \lambda R[\mathbf{T}] \quad (20)$$

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Properties of our Lagrangian:

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$$\mathcal{L}[\boldsymbol{\kappa}, \mathbf{c}, \mathcal{E}_0, \mathbf{d}, \lambda_{\mathbf{c}}, \lambda_{\mathbf{d}}] = E_0[\boldsymbol{\kappa}, \mathbf{c}, \mathcal{E}_0] + E_2[\boldsymbol{\kappa}, \mathbf{c}, \mathbf{d}] + \lambda_{\mathbf{c}}^\dagger \frac{\partial E_0}{\partial \mathbf{c}^\dagger} + \lambda_{\mathbf{d}}^\dagger \frac{\partial E_2}{\partial \mathbf{d}^\dagger} \quad (24)$$

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$$\frac{\partial L}{\partial \boldsymbol{\kappa}} = \sum_{ijkl} \frac{\partial H_{0,ijkl}}{\partial \boldsymbol{\kappa}} \Gamma_{ijkl}^{c,c} + \frac{\partial H_{0,ijkl}}{\partial \boldsymbol{\kappa}} \Gamma_{ijkl}^{d,d} + 2 \frac{\partial V_{ijkl}}{\partial \boldsymbol{\kappa}} \Gamma_{ijkl}^{d,c} + 2 \frac{\partial H_{0,ijkl}}{\partial \boldsymbol{\kappa}} \Gamma_{ijkl}^{\lambda_c, c} \quad (25)$$

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Connecting to PySCF: Overview

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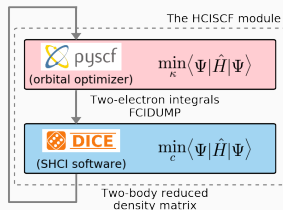


Figure 6: Overview of workflow for HCISCF module from Smith et al. 2017

Running the calculations

1. Run HCISCF to generate multiconfigurational orbitals
2. Run final SHCI calculation w/ tight settings (more determinants) to get final energy

Applications

Fe(porphyrin): Motivation

- Model system for active site of heme group

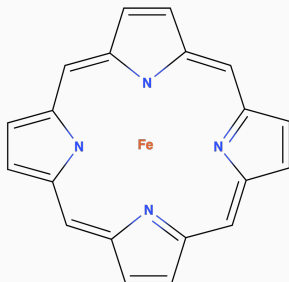


Figure 7: Fe(II)(porphyrin)

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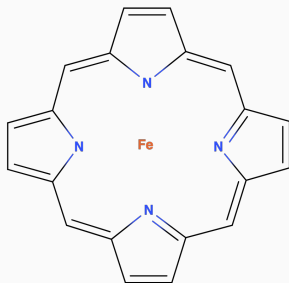


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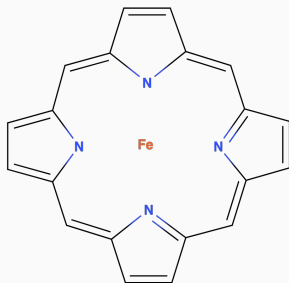


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- Test impact of PT correction in HCISCF

Fe(porphyrin): Motivation

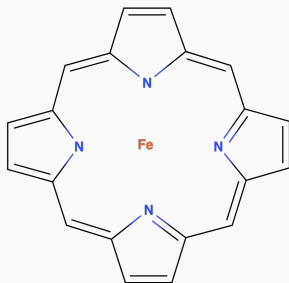


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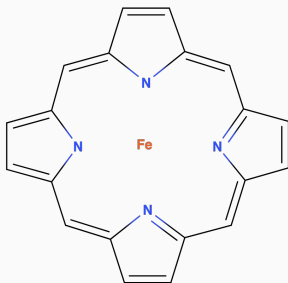


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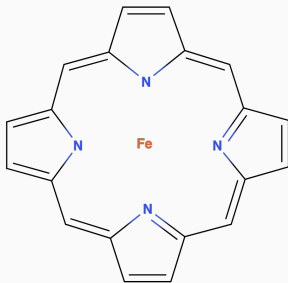


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- Almost all theoretical work suggests $^5A_{1g}$

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	ϵ_1 (Ha)	E_{HCISCF} (Ha)	E_{SHCI} (Ha)
vHCISCF	1×10^{-4}	-2244.9980	-2245.0314
vHCISCF	5×10^{-5}	-2245.0121	-2245.0313
HCISCF	5×10^{-5}	-2245.0178	-2245.0314

Other Theoretical Work

E_{ex} (kcal/mol)	Method	Active Space	Reference
20.3	CASSCF (6e,5o)	Fe 3d	Pierloot 2002
9.4	CASSCF (8e,11o)	Fe 3d, 3d', σ Fe-N	Pierloot 2002
16.4	CASSCF (8e,11o)	Fe 3d, Fe 3d', Fe-N σ	Phung 2016
20.0	CASSCF (14e,13o)	Fe 3d, 4 π	Pierloot 2002
-13.0	DMRGCI (44e,44o)	Fe 3/4d, 4px/y, π , N 2px/y	Ghosh 2015
12.2	CASPT2 (6e,5o)	Fe 3d	Pierloot 2002
4.9	CASPT2 (8e,11o)	Fe 3d, 3d', σ Fe-N	Pierloot 2002
12.1	CASPT2 (14e,13o)	Fe 3d, 4 π	Pierloot 2002
-0.9	CASPT2 (16e,15o)	Fe 3d, 3d', 3s, 3p, Fe-N σ	Vancoillie 2011

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

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

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Basis	Sym.	E_{vHCISCF} (Ha)	E_{SHCI} (Ha)	E_{ex} (kcal/mol)	T_{OO} (sec)	T_{CI} (sec)
cc-pVDZ	5A_g	-2244.9980	-2245.0314(5)	16.7	126	52
cc-pVDZ	$^3B_{1g}$	-2244.9776	-2245.0049(6)		114	56
cc-pVTZ	5A_g	-2245.2229	-2245.2549(5)	16.4	2236	70
cc-pVTZ	$^3B_{1g}$	-2245.1958	-2245.2288(6)		2270	98

Fe(porphyrin): What now?

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cc-pVDZ	5A_g	-2245.1457	-2245.1964(9)	-2.0	277	185
cc-pVDZ	$^3B_{1g}$	-2245.1567	-2245.1995(6)		264	147

Conclusion and Future Work

Conslusions

Wrap up:

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Up next:

- Adding out-of-active space dynamical correlation (NEVPT/MRLCC)
- Using machine learning to grow variational space even more intelligently

Acknowledgements

Thanks to Sandeep Sharma, Bastien Mussard, and Adam Holmes for putting up with all my questions and offering countless helpful advice. This work was supported by Sandeep's startup grant and the GAANN Fellowship.

Questions

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

Pentacene: Motivation

- Radical character of linear acenes increases with chain length
- Linear acenes used frequently in singlet fission, want predictive accuracy

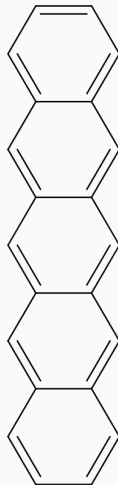


Figure 8:

Pentacene: Comparing vHCISCF and HCISCF

	ϵ_1 (Ha)	E_{HCISCF} (Ha)	E_{SHCI} (Ha)
vHCISCF	8.5×10^{-5}	-841.5936	-841.6174
vHCISCF	5.0×10^{-5}	-841.6005	-841.6175
HCISCF	8.5×10^{-5}	-841.6021	-841.6173

Pentacene: Calculations

Sym.	E_{vHCISCF} (Ha)	E_{SHCI} (Ha)	E_{ex} (kcal/mol)	E_{ref} (kcal/mol)	T_{OO} (sec)	T_{CI} (sec)
Singlet Geometry						
$^1A_{\text{g}}$	-841.5936	-841.6174(6)	28.5	27.0	50	33
$^3B_{2\text{u}}$	-841.5457	-841.5720(8)			70	24
Triplet Geometry						
$^1A_{\text{g}}$	-841.5823	-841.6050(7)	18.6	-	57	26
$^3B_{2\text{u}}$	-841.5556	-841.5751(9)			57	31

Pentacene: Calculations

- Orbital optimization is the rate limiting step in these calculations
- Not as close to the other theoretical work as we'd like for singlet geometry (maybe b/c small basis difference)
- Triplet geometry w/in c.a. 1 kcal/mole of experimental gap

References



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