

# Sessions: Methods based on selection and/or stochastic sampling of parts of Hilbert space

Sandeep Sharma  
University of Colorado, Boulder  
February 11, 2021

Work on wave-function methods in quantum chemistry and  
nuclear physics  
Laboratoire de Chimie Theorique (LCT)

# Outline

- Can free propagation work to get exact answers  
*(~50 electrons)*
- Multireference methods
  - Selected configuration interaction *(~20 electrons)*
  - Multireference perturbation theory *(>100 electrons)*

# Free propagation



Ankit Mahajan

# Imaginary time propagation (cooling the system)

$$-\frac{\partial|\Psi\rangle}{\partial\tau} = H|\Psi\rangle$$

where  $\tau = it$

*same role as inverse temperature  
(we are cooling the system)*

$$|\Psi(\tau)\rangle = e^{-\tau H}|\Psi(0)\rangle$$

*for large enough  $\tau$  one gets  
the ground state*

# Imaginary time propagation (cooling the system)

$$-\frac{\partial|\Psi\rangle}{\partial\tau} = H|\Psi\rangle$$

where  $\tau = it$

*same role as inverse temperature  
(we are cooling the system)*

$$|\Psi(\tau)\rangle = e^{-\tau H}|\Psi(0)\rangle$$

*for large enough  $\tau$  one gets  
the ground state*

If

$$|\Psi(0)\rangle = c_0|\Phi_0\rangle + c_1|\Phi_1\rangle + c_2|\Phi_2\rangle + \dots$$

then

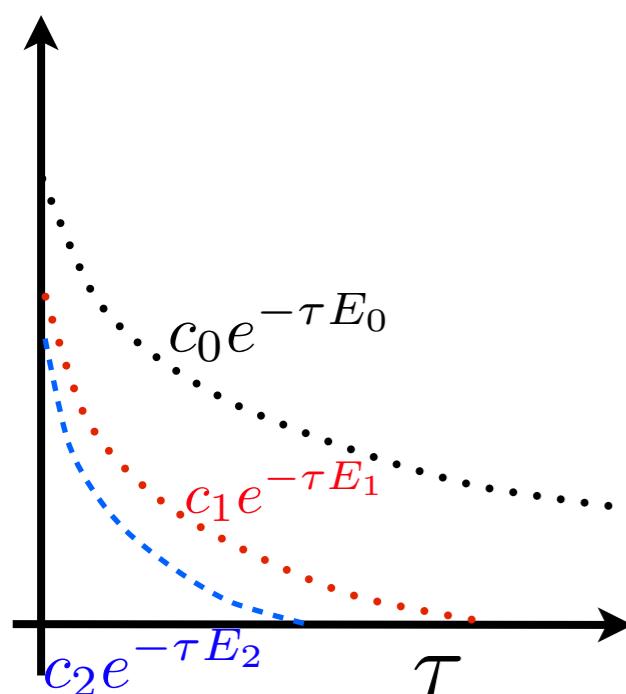
$$|\Psi(\tau)\rangle = c_0e^{-\tau E_0}|\Phi_0\rangle + c_1e^{-\tau E_1}|\Phi_1\rangle + c_2e^{-\tau E_2}|\Phi_2\rangle + \dots$$

# Imaginary time propagation (cooling the system)

$$-\frac{\partial|\Psi\rangle}{\partial\tau} = H|\Psi\rangle$$

where  $\tau = it$

*same role as inverse temperature  
(we are cooling the system)*



$$|\Psi(\tau)\rangle = e^{-\tau H}|\Psi(0)\rangle$$

*for large enough  $\tau$  one gets  
the ground state*

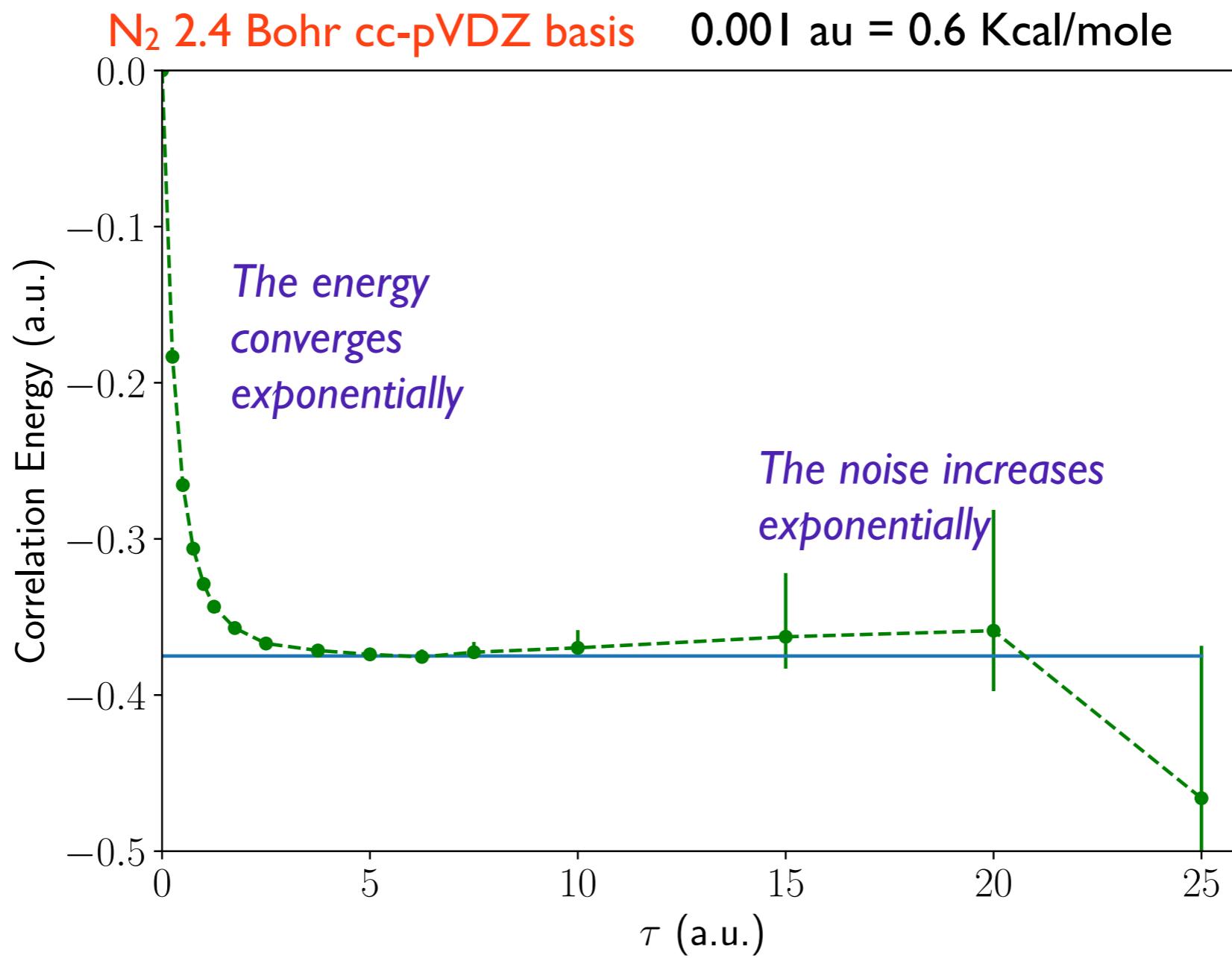
If  $|\Psi(0)\rangle = c_0|\Phi_0\rangle + c_1|\Phi_1\rangle + c_2|\Phi_2\rangle + \dots$

then  $|\Psi(\tau)\rangle = c_0e^{-\tau E_0}|\Phi_0\rangle + c_1e^{-\tau E_1}|\Phi_1\rangle + c_2e^{-\tau E_2}|\Phi_2\rangle + \dots$

# Can we use it? (Sort of)

We cannot do it deterministically.

Can use Stochastic methods (via a trick called Hubbard-Stratonovich transformation)



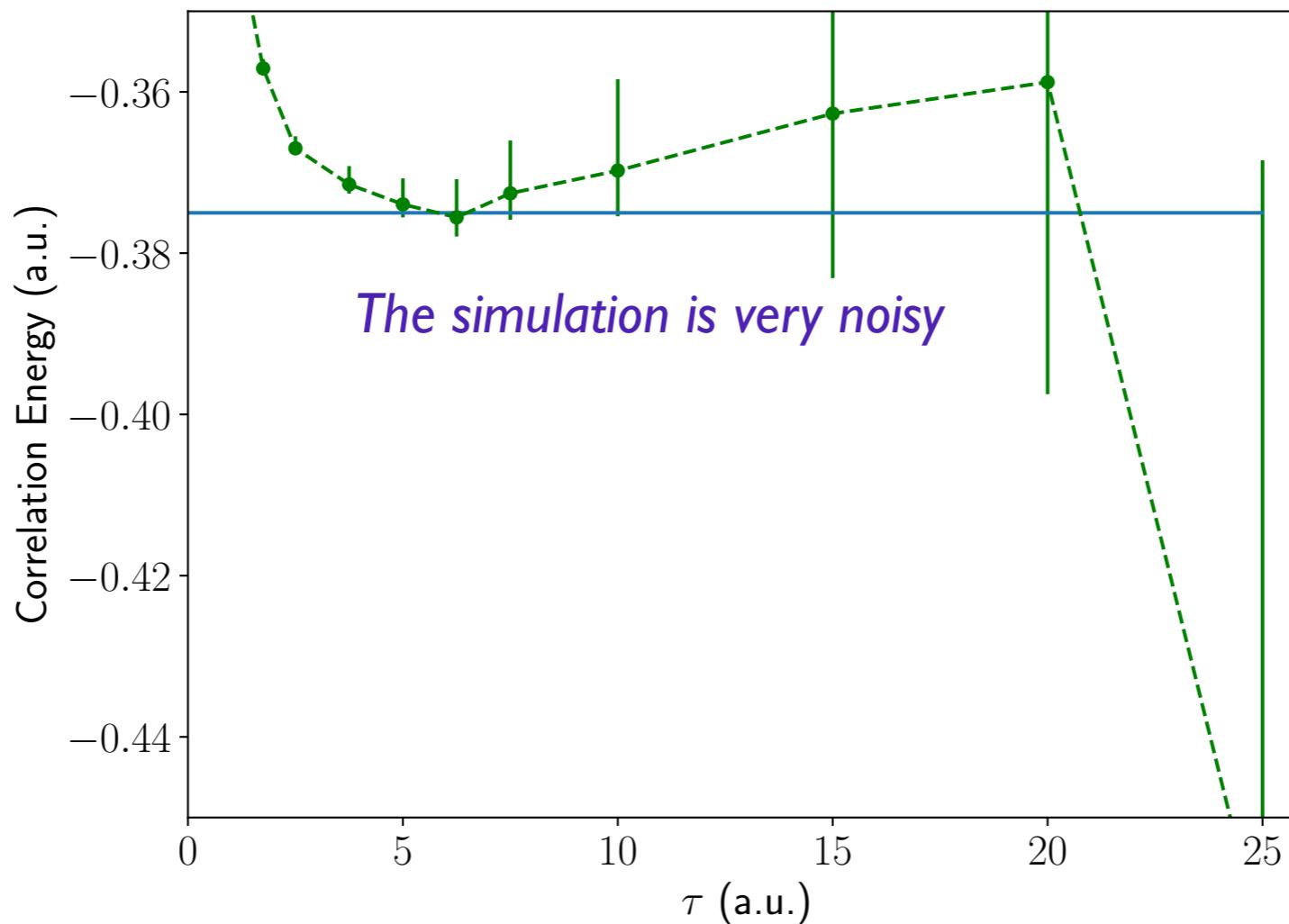
$$\frac{\langle \Psi_A | H e^{-\tau H} | \Psi(0) \rangle}{\langle \Psi_A | e^{-\tau H} | \Psi(0) \rangle}$$

# Can we use it? (Sort of)

We cannot do it deterministically.

Can use Stochastic methods (via a trick called Hubbard-Stratonovich transformation)

N<sub>2</sub> 2.4 Bohr cc-pVDZ basis    0.001 au = 0.6 Kcal/mole



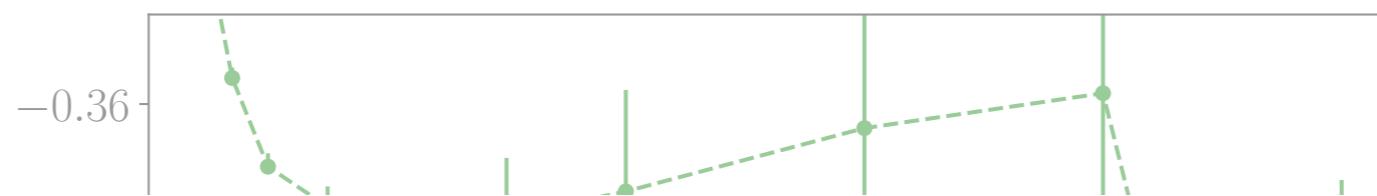
$$\frac{\langle \Psi_A | H e^{-\tau H} | \Psi(0) \rangle}{\langle \Psi_A | e^{-\tau H} | \Psi(0) \rangle}$$

# Can we use it? (Sort of)

We cannot do it deterministically.

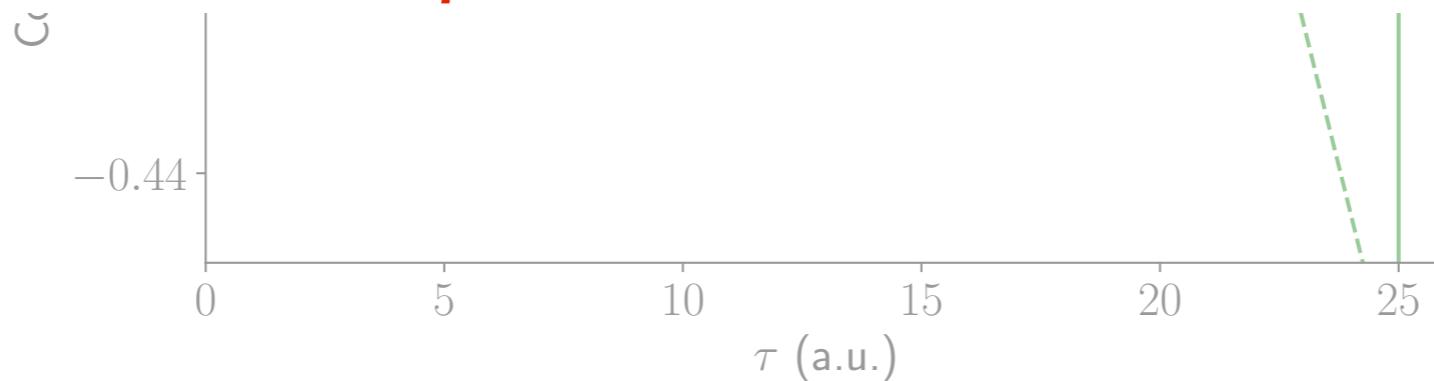
Can use Stochastic methods (via a trick called Hubbard-Stratonovich transformation)

$N_2$  2.4 Bohr cc-pVDZ basis     $0.001 \text{ au} = 0.6 \text{ Kcal/mole}$



## This is the famous sign problem!!!

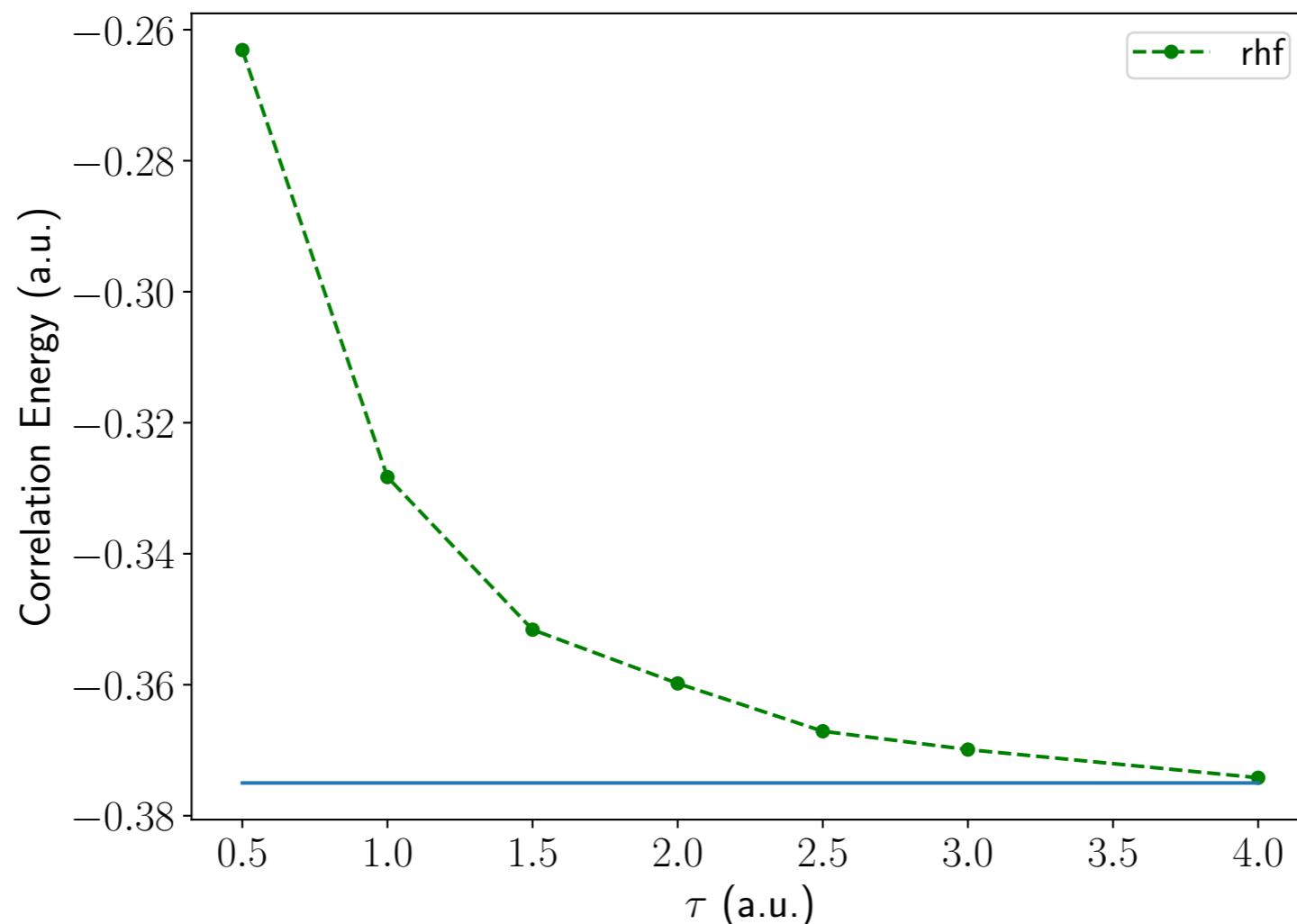
Most algorithms introduce constraints (bias) e.g  
DMC,  $c\bar{p}$ -AFQMC, GFMC, FCIQMC etc



# Can we do better

We can chose to use better initial state

N<sub>2</sub> 2.4 Bohr cc-pVDZ basis    0.001 au = 0.6 Kcal/mole



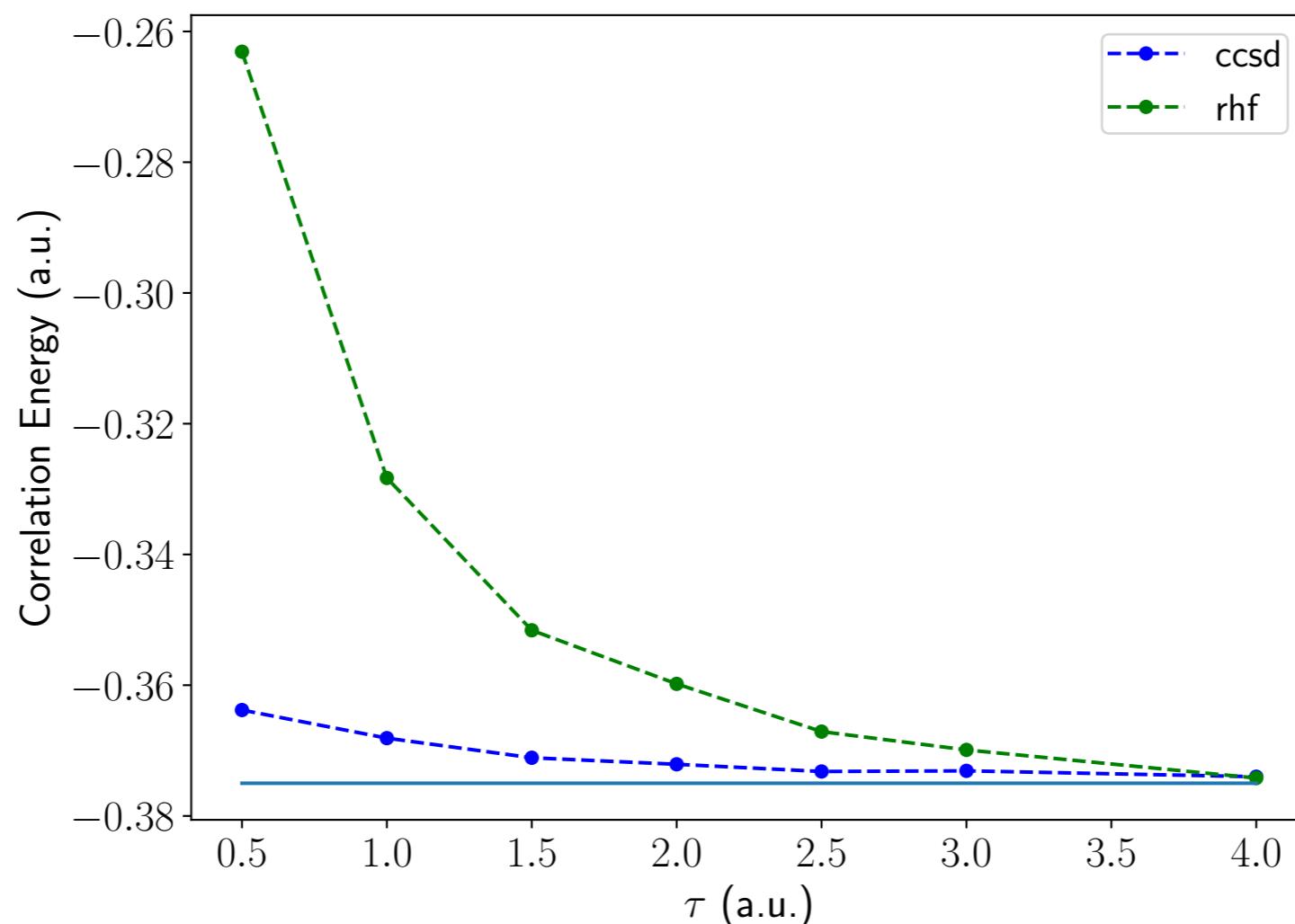
$$|\Psi(0)\rangle = c_0 |\Phi_0\rangle + c_1 |\Phi_1\rangle + c_2 |\Phi_2\rangle + \dots$$

$$|\Psi(\tau)\rangle = c_0 e^{-\tau E_0} |\Phi_0\rangle + c_1 e^{-\tau E_1} |\Phi_1\rangle + c_2 e^{-\tau E_2} |\Phi_2\rangle + \dots$$

# Can we do better

We can chose to use better initial state

N<sub>2</sub> 2.4 Bohr cc-pVDZ basis    0.001 au = 0.6 Kcal/mole



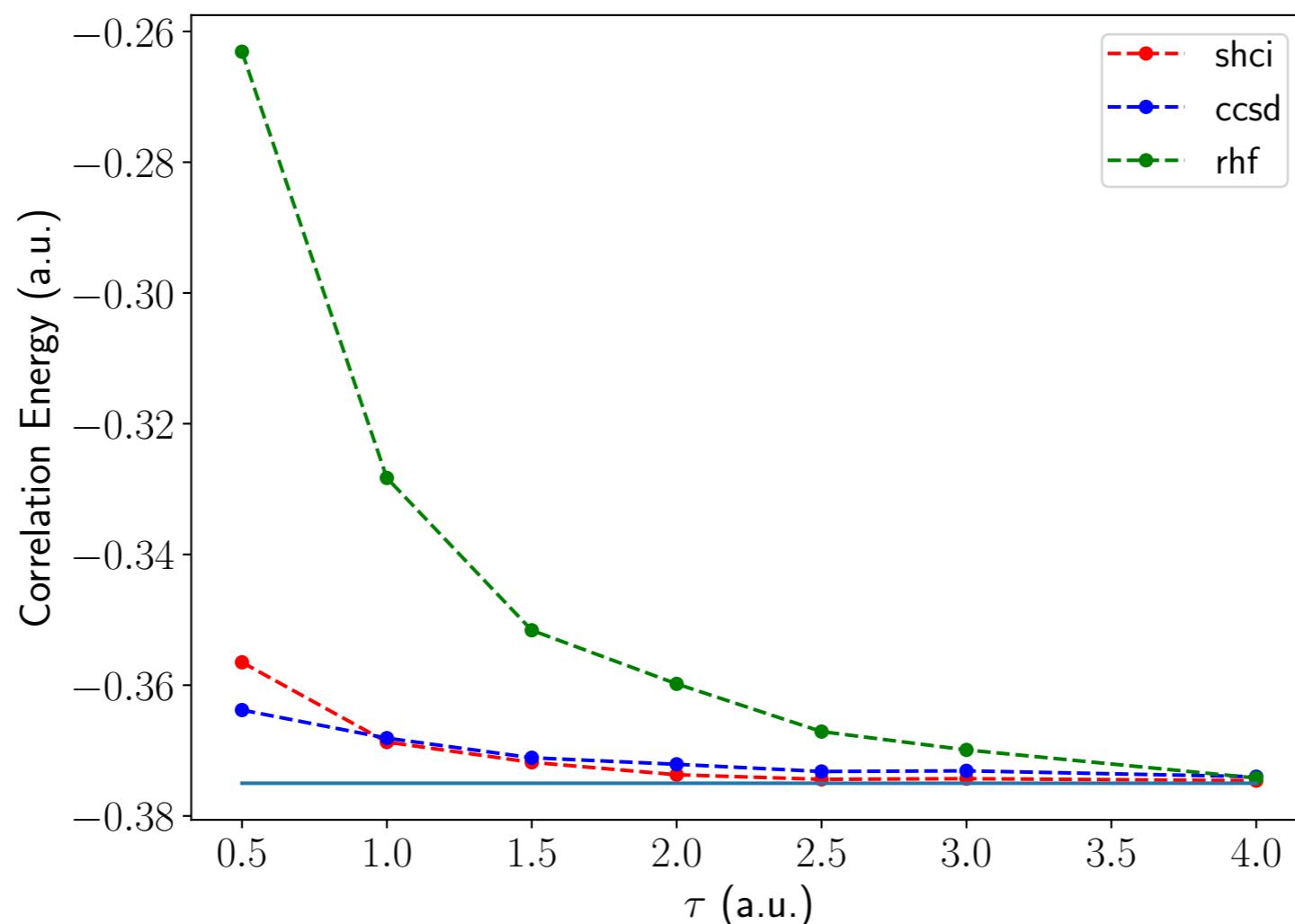
$$|\Psi(0)\rangle = c_0 |\Phi_0\rangle + c_1 |\Phi_1\rangle + c_2 |\Phi_2\rangle + \dots$$

$$|\Psi(\tau)\rangle = c_0 e^{-\tau E_0} |\Phi_0\rangle + c_1 e^{-\tau E_1} |\Phi_1\rangle + c_2 e^{-\tau E_2} |\Phi_2\rangle + \dots$$

# Can we do better

We can chose to use better initial state

N<sub>2</sub> 2.4 Bohr cc-pVDZ basis    0.001 au = 0.6 Kcal/mole



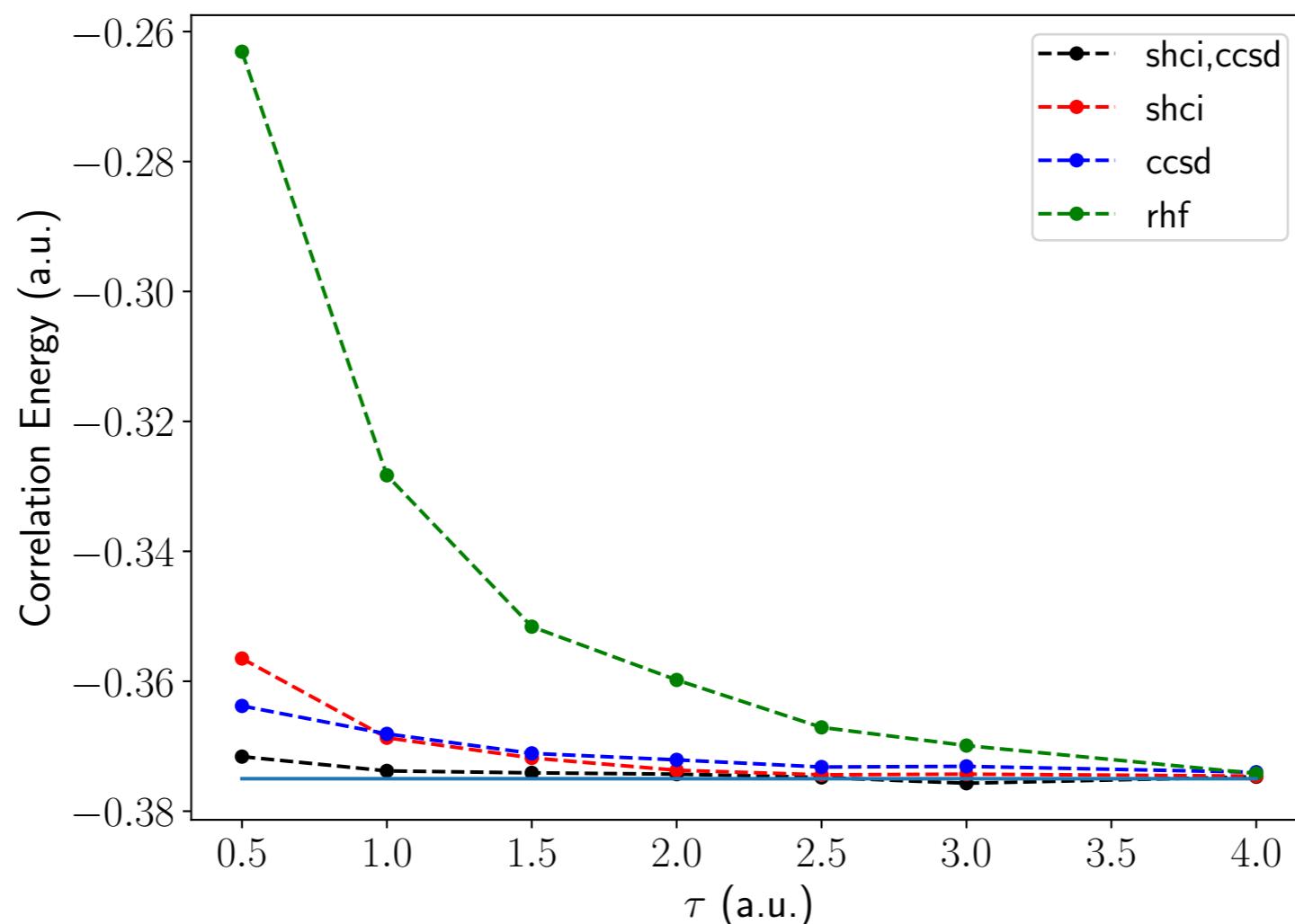
$$|\Psi(0)\rangle = c_0 |\Phi_0\rangle + c_1 |\Phi_1\rangle + c_2 |\Phi_2\rangle + \dots$$

$$|\Psi(\tau)\rangle = c_0 e^{-\tau E_0} |\Phi_0\rangle + c_1 e^{-\tau E_1} |\Phi_1\rangle + c_2 e^{-\tau E_2} |\Phi_2\rangle + \dots$$

# Can we do better

We can chose to use better initial state

N<sub>2</sub> 2.4 Bohr cc-pVDZ basis    0.001 au = 0.6 Kcal/mole



$$\frac{\langle \Psi_A | H e^{-\tau H} | \Psi(0) \rangle}{\langle \Psi_A | e^{-\tau H} | \Psi(0) \rangle}$$

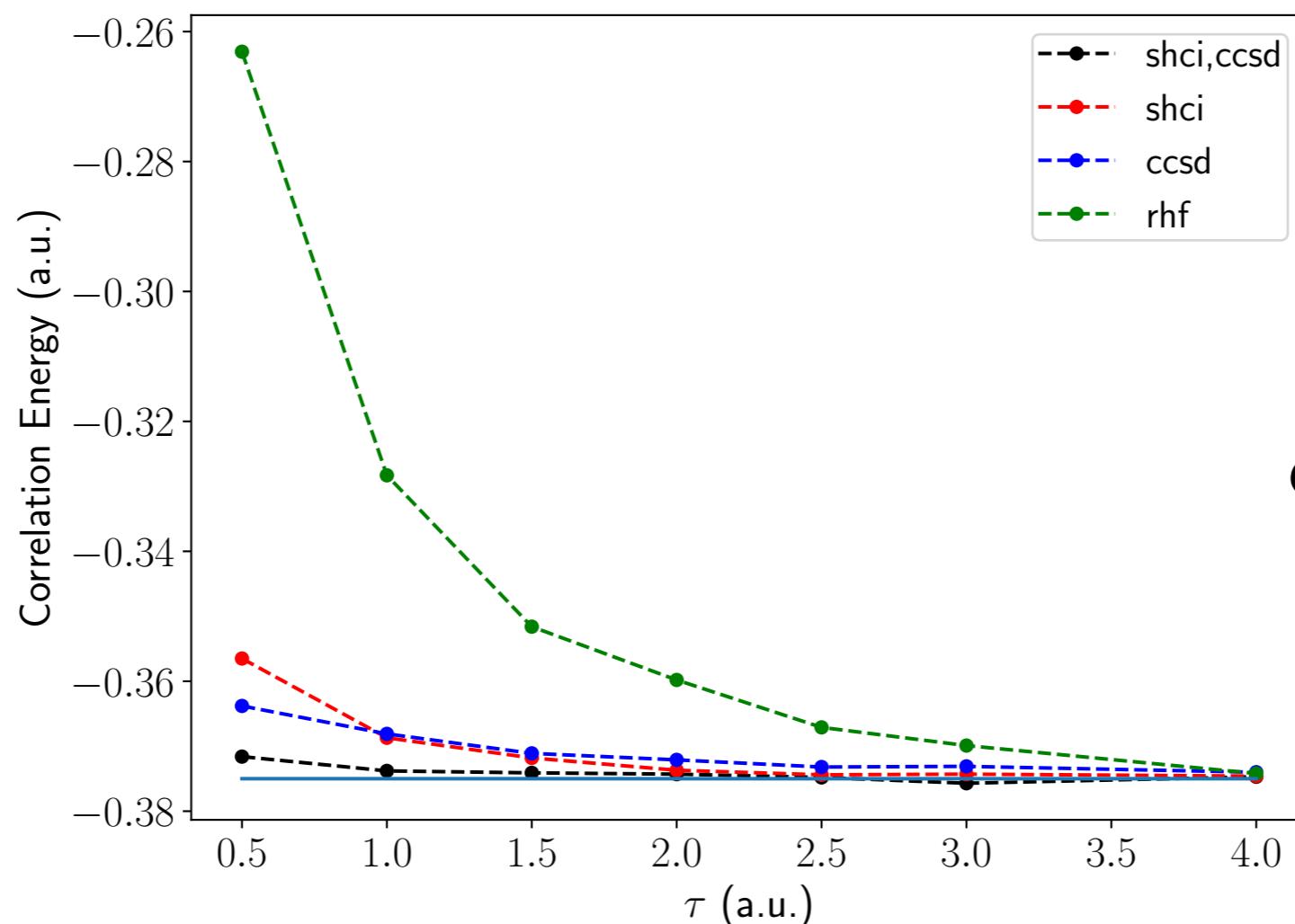
$$|\Psi(0)\rangle = c_0 |\Phi_0\rangle + c_1 |\Phi_1\rangle + c_2 |\Phi_2\rangle + \dots$$

$$|\Psi(\tau)\rangle = c_0 e^{-\tau E_0} |\Phi_0\rangle + c_1 e^{-\tau E_1} |\Phi_1\rangle + c_2 e^{-\tau E_2} |\Phi_2\rangle + \dots$$

# Can we do better

We can chose to use better initial state

N<sub>2</sub> 2.4 Bohr cc-pVDZ basis    0.001 au = 0.6 Kcal/mole



$$\frac{\langle \Psi_A | H e^{-\tau H} | \Psi(0) \rangle}{\langle \Psi_A | e^{-\tau H} | \Psi(0) \rangle}$$

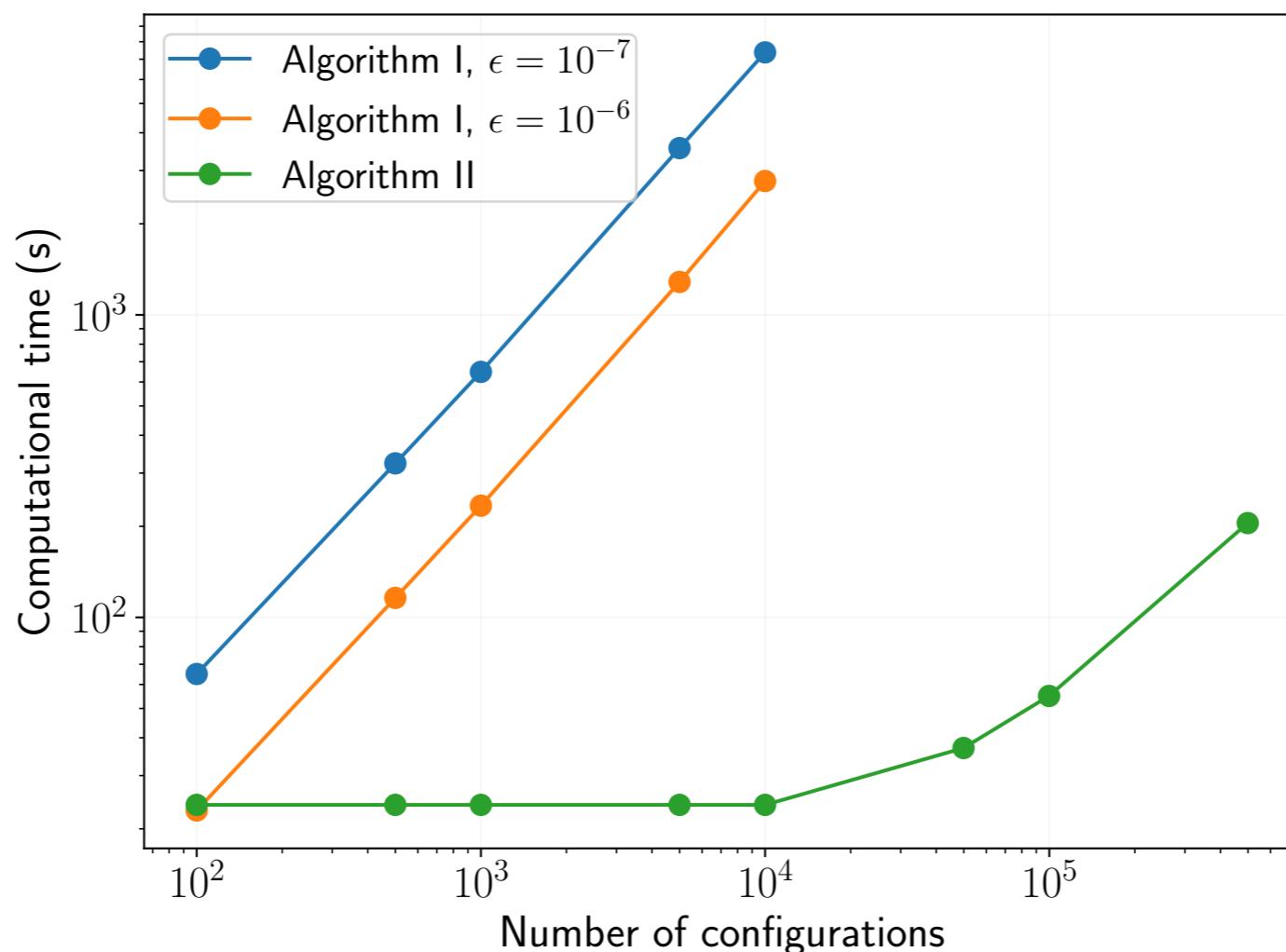
JCP, 152, 2020, 194108

Generalization of Filippi, Assaraf  
algorithm

$$|\Psi(0)\rangle = c_0 |\Phi_0\rangle + c_1 |\Phi_1\rangle + c_2 |\Phi_2\rangle + \dots$$

$$|\Psi(\tau)\rangle = c_0 e^{-\tau E_0} |\Phi_0\rangle + c_1 e^{-\tau E_1} |\Phi_1\rangle + c_2 e^{-\tau E_2} |\Phi_2\rangle + \dots$$

# Dealing with multislater wavefunctions



JCP, 152, 2020, 194108

Generalization of Filippi, Assaraf algorithm (JCP, 144, 2016, 194105)

# What about basis set ( $\text{H}_2\text{O}$ )

*For every cardinal number (DZ, TZ, QZ) the cost increases by about a factor of 8.*

# What about basis set ( $\text{H}_2\text{O}$ )

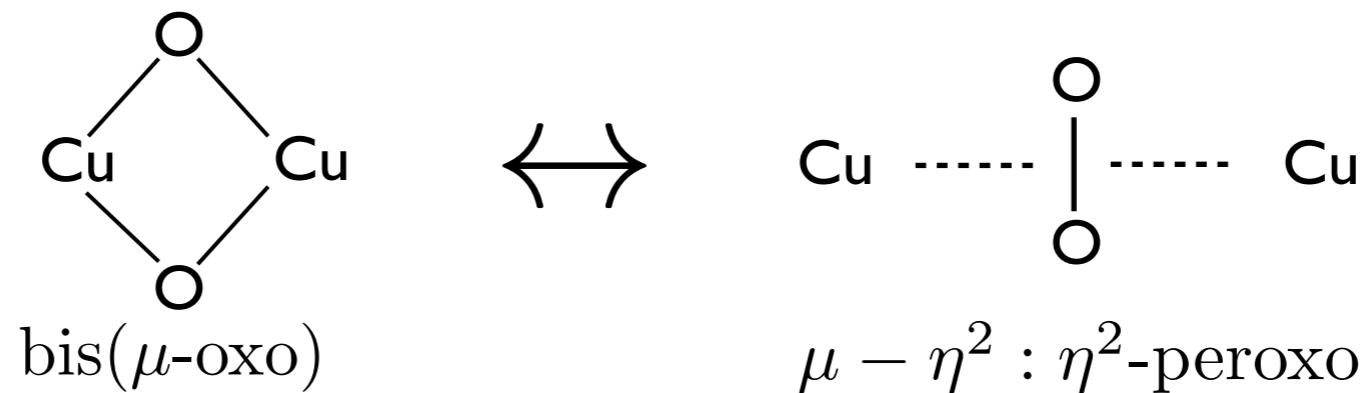
*For every cardinal number (DZ, TZ, QZ) the cost increases by about a factor of 8.*

Time	TZ-DZ	QZ-TZ
0.5	-0.1008	-0.0967
1.0	-0.1011	-0.1000
1.5	-0.1017	-0.1025
2.0	-0.1006	-0.1023

*The energies change almost in parallel*

# Lets do something a bit more challenging

*Cu-Oxygen complexes in biology and synthetic chemistry are used for C-H bond activation.*



(32e, 108o)

Hilbert space -  $10^{40}$

18 hours on 4 nodes

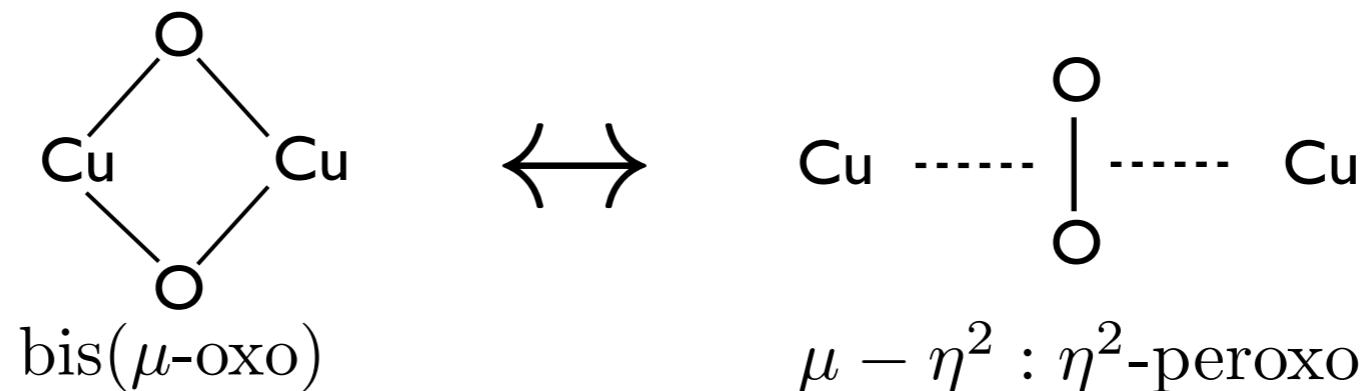
Chem Rev, 104, 2004, 1013

Chem Rev, 104, 2004, 1047

Chem Rev, 117, 2017, 2059

# Lets do something a bit more challenging

*Cu-Oxygen complexes in biology and synthetic chemistry are used for C-H bond activation.*



(32e, 108o)

Hilbert space -  $10^{40}$

18 hours on 4 nodes

Method	Kcal/mole
MP2	29
CCSD	41
CCSD(T)	30
CASPT2 (16,14)	1
B3LYP	52
fp-AFQMC	25 (1)

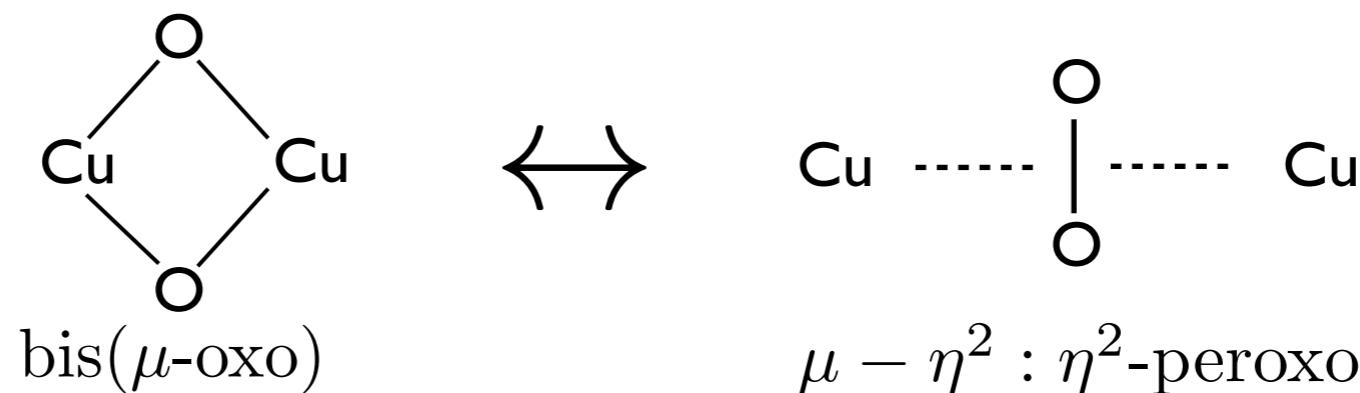
Chem Rev, 104, 2004, 1013

Chem Rev, 104, 2004, 1047

Chem Rev, 117, 2017, 2059

# Lets do something a bit more challenging

*Cu-Oxygen complexes in biology and synthetic chemistry are used for C-H bond activation.*



(32e, 108o)

Hilbert space -  $10^{40}$

18 hours on 4 nodes

(52e, 108o)

Hilbert space -  $10^{50}$

x7

Chem Rev, 104, 2004, 1013

Chem Rev, 104, 2004, 1047

Chem Rev, 117, 2017, 2059

Method	Kcal/mole
MP2	29
CCSD	41
CCSD(T)	30
CASPT2 (16,14)	1
B3LYP	52
fp-AFQMC	25 (1)

# Cholesky decomposition/density fitting

$$H = K + V$$

$$\begin{aligned} V &= \sum_{ijkl} (ij|kl) a_i^\dagger a_j a_k^\dagger a_l = \sum_\gamma \sum_{ijkl} (ij|\gamma)(kl|\gamma) a_i^\dagger a_j a_k^\dagger a_l \\ &= \sum_\gamma \left( \sum_{ij} (ij|\gamma) a_i^\dagger a_j \right) \left( \sum_{kl} (kl|\gamma) a_k^\dagger a_l \right) \\ &= \sum_\gamma v_\gamma^2 \end{aligned}$$

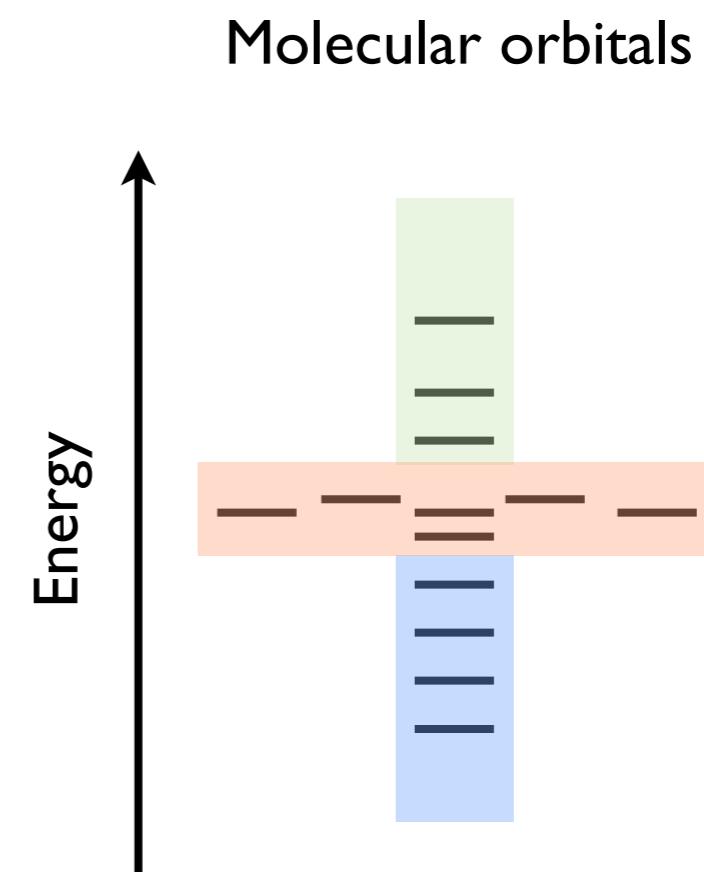
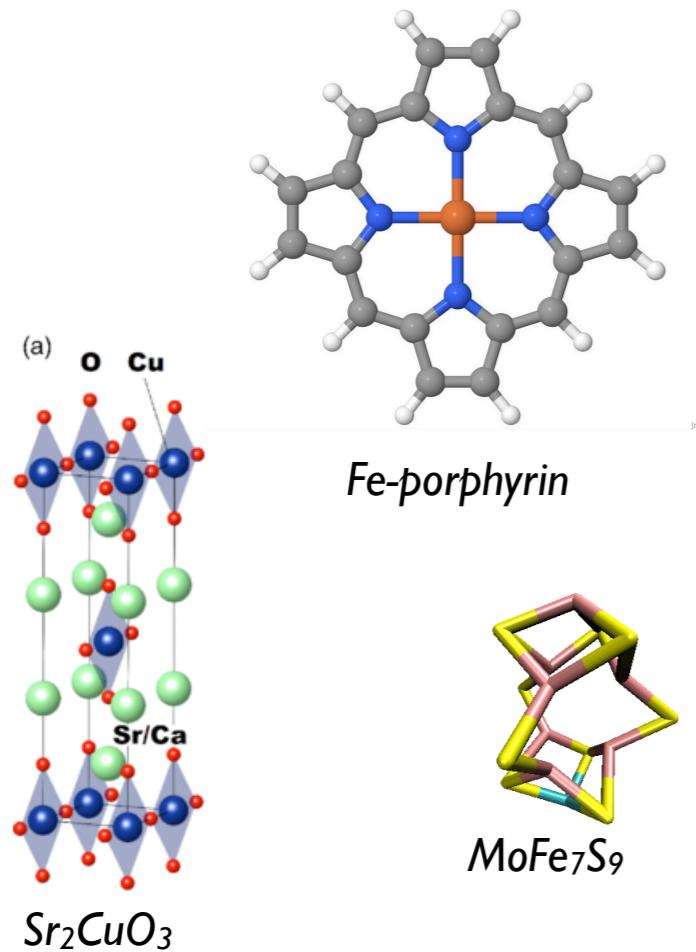
$$\exp(-\Delta\tau v^2) = \int dx e^{-\frac{x^2}{2}} \exp(x\sqrt{-\Delta\tau}v)$$

# Hubbard Stratonovich

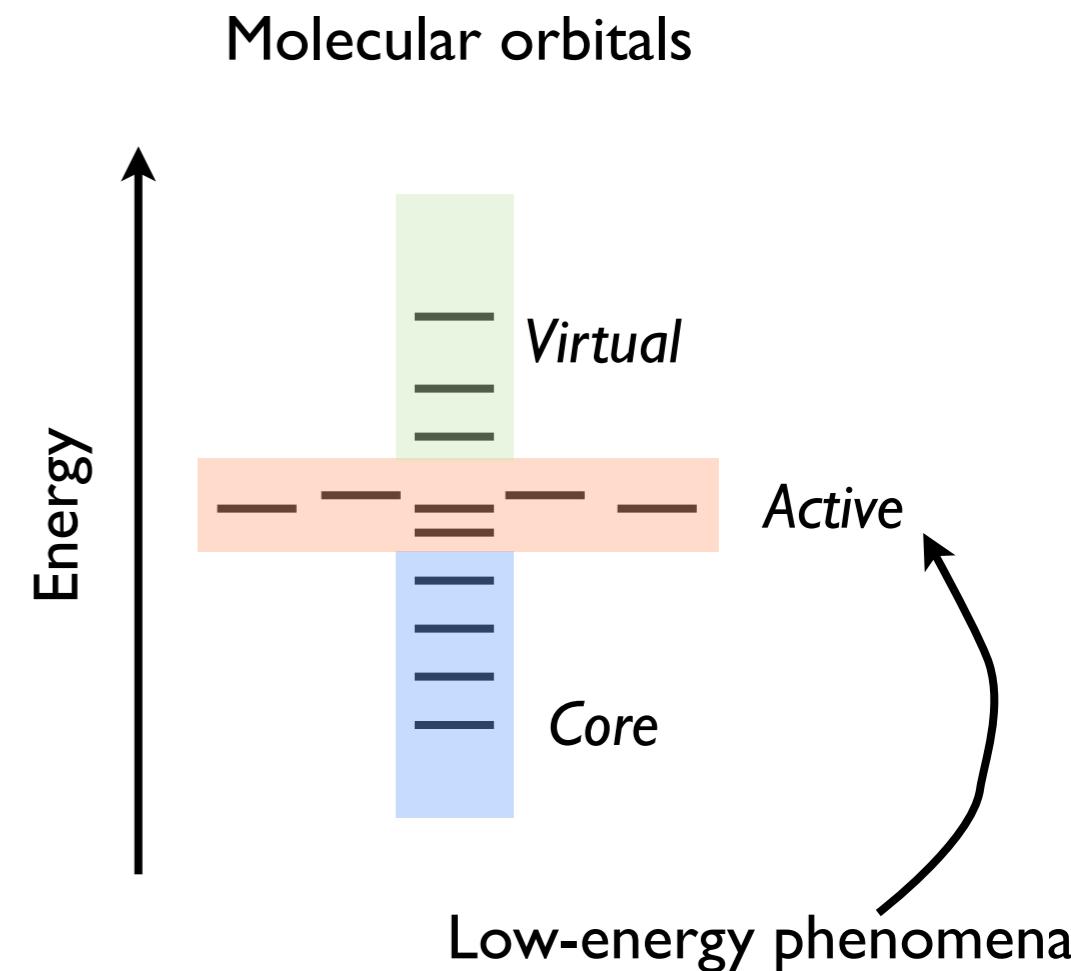
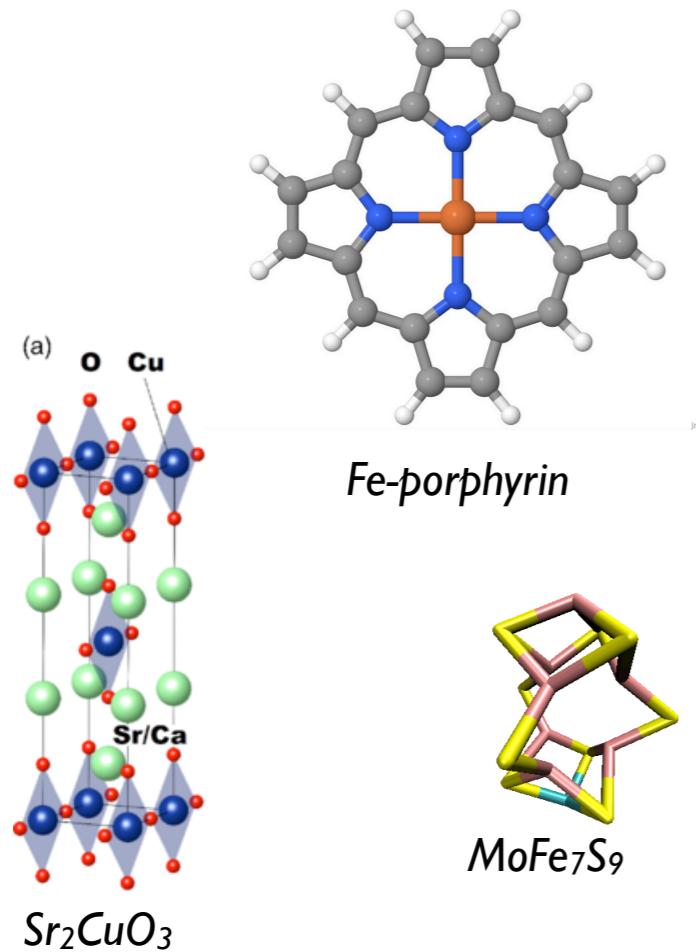
$$\begin{aligned} U(\tau) &= \exp(-\tau H) = \exp(-\Delta\tau H)^N \\ &= \left( \exp\left(-\frac{\Delta\tau}{2}K\right) \exp(-\Delta\tau V) \exp\left(-\frac{\Delta\tau}{2}K\right) \right)^N + O(\Delta\tau^2) \\ &= \left( \prod_{\gamma} \int \frac{dx_{\gamma}}{\sqrt{2\pi}} e^{-\frac{x_{\gamma}^2}{2}} \exp\left(-\frac{\Delta\tau}{2}K\right) \exp\left(-\sum_{\gamma} x_{\gamma} \sqrt{-\Delta\tau} v_{\gamma}\right) \exp\left(-\frac{\Delta\tau}{2}K\right) \right)^N + O(\Delta\tau) \\ &= \prod_{l=1}^N \int d\mathbf{x}_l p(\mathbf{x}_l) B(\mathbf{x}_l) + O(\Delta\tau) \end{aligned}$$

# Multireference methods

# Nomenclature and background

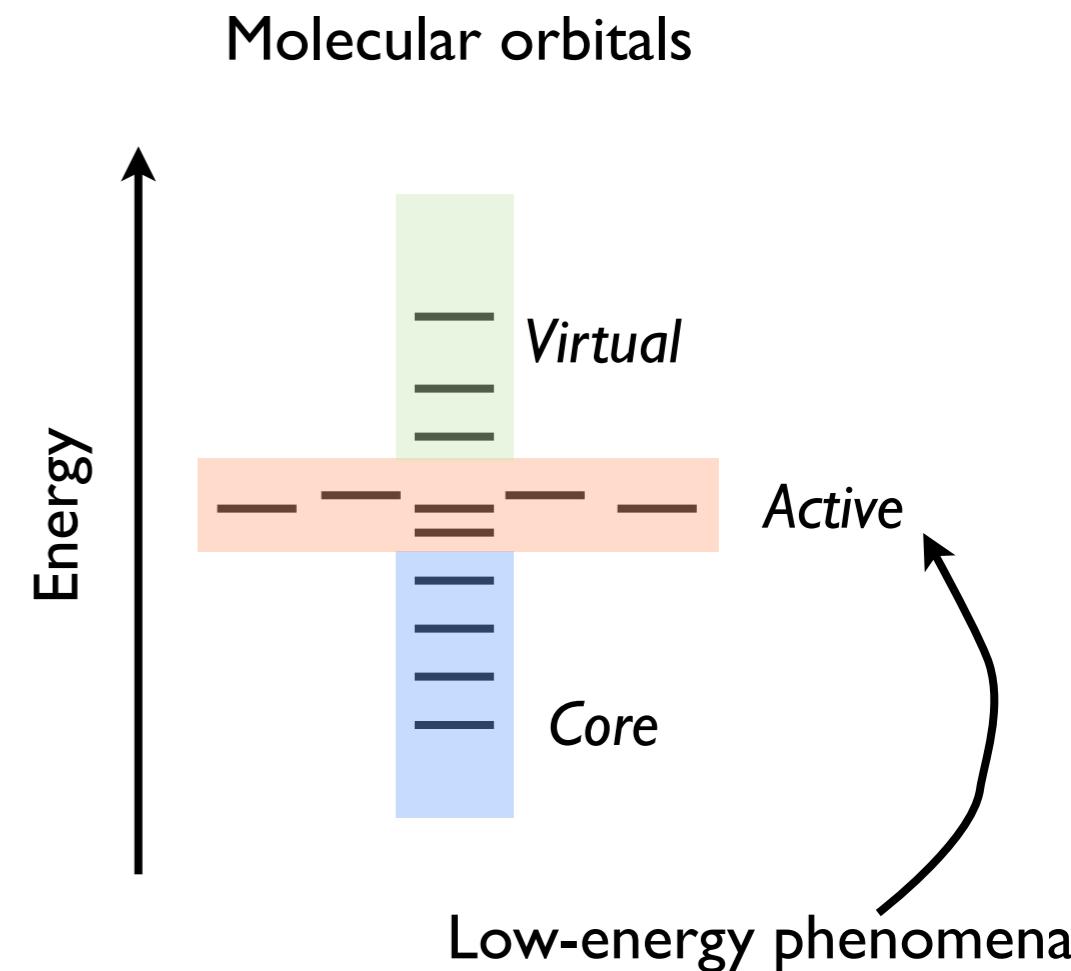
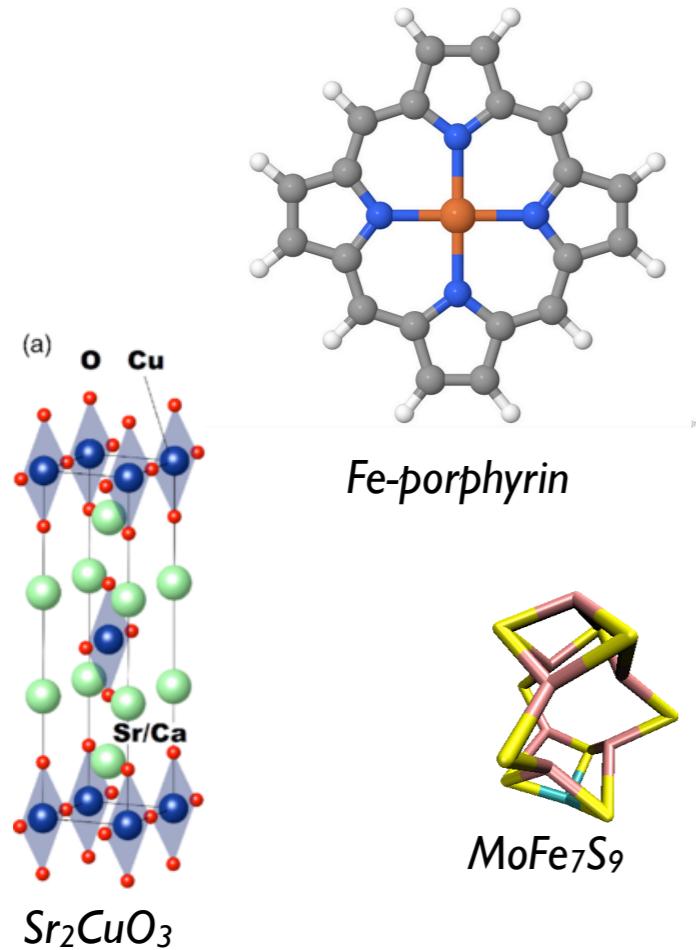


# Nomenclature and background



- Low energy effective Hamiltonian lives in the active space
- Correlation in active space: *strong correlation, static correlation*

# Nomenclature and background



- Low energy effective Hamiltonian lives in the active space
- Correlation in active space: *strong correlation, static correlation*
- Other electrons and orbitals play a role in screening: weak correlation, dynamical correlation

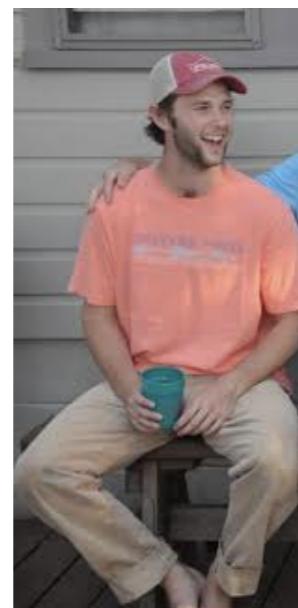
# Active space FCI



Cyrus Umrigar



Adam Holmes

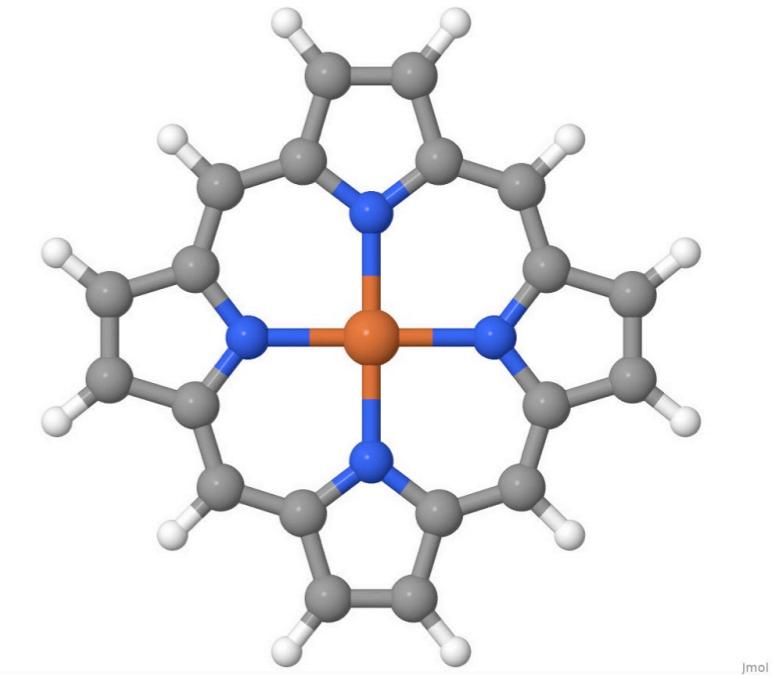
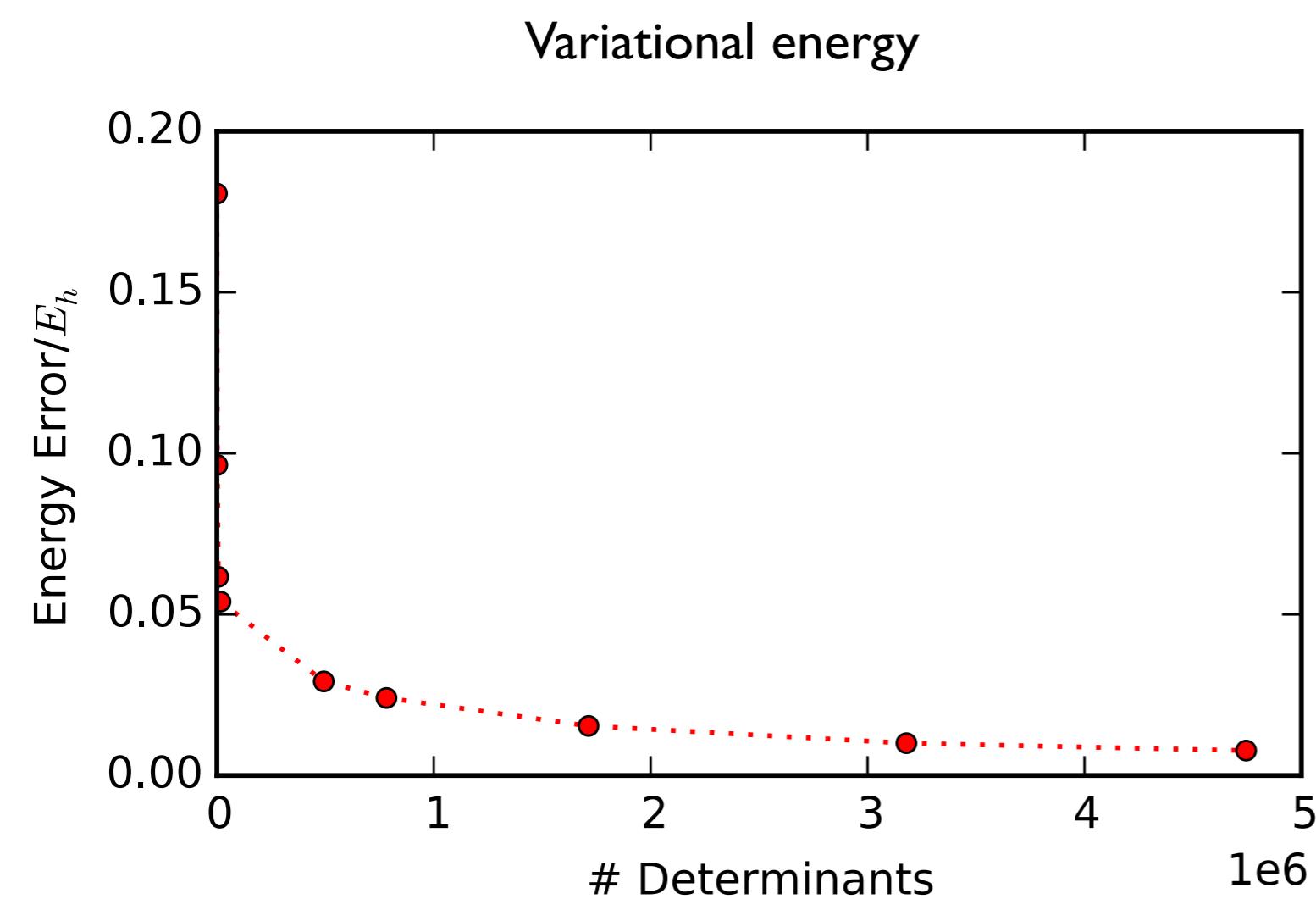


James Smith



Xubo Wang

# Useful Observation

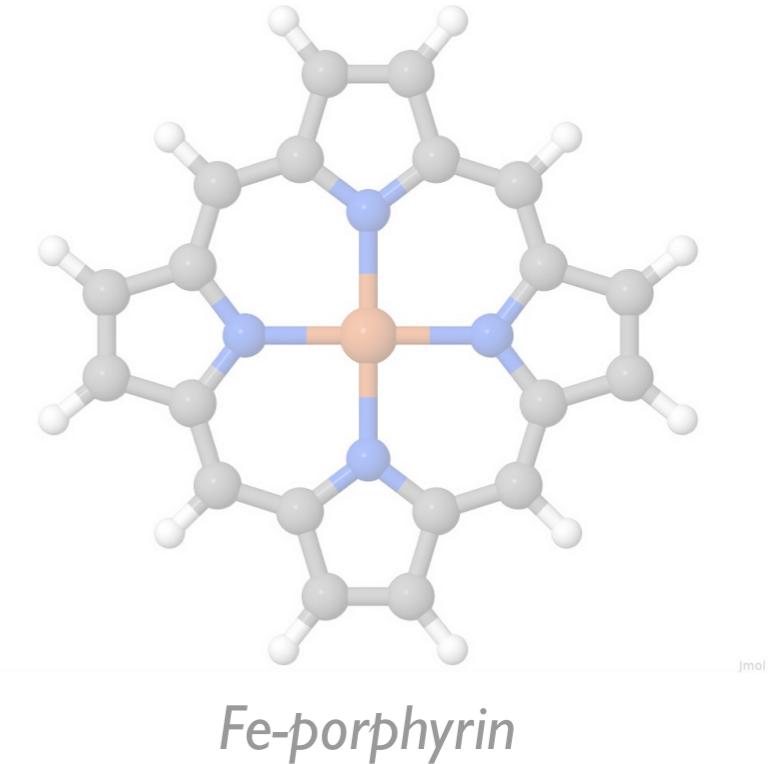
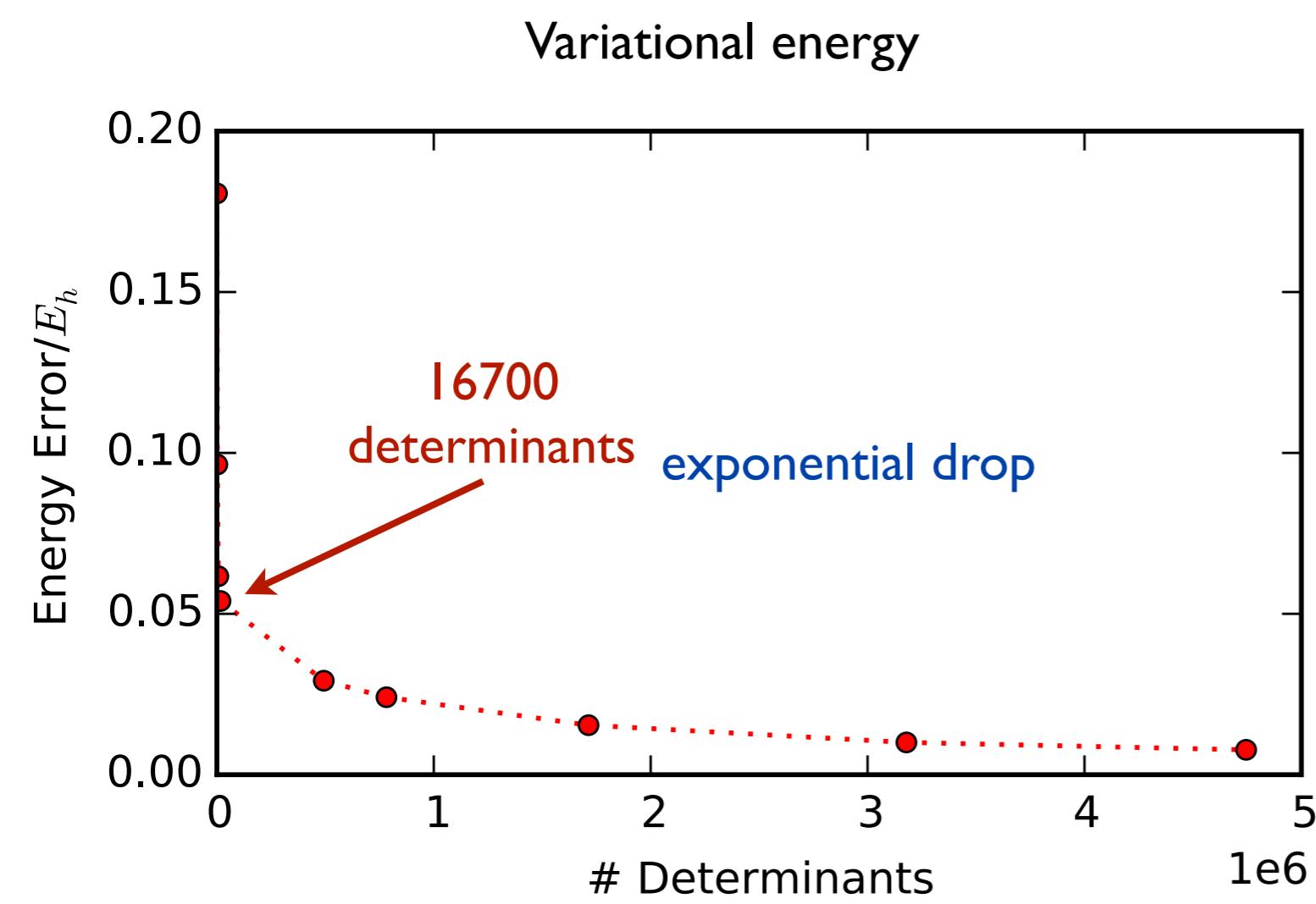


*Fe-porphyrin*

Active space - (32e, 29o)

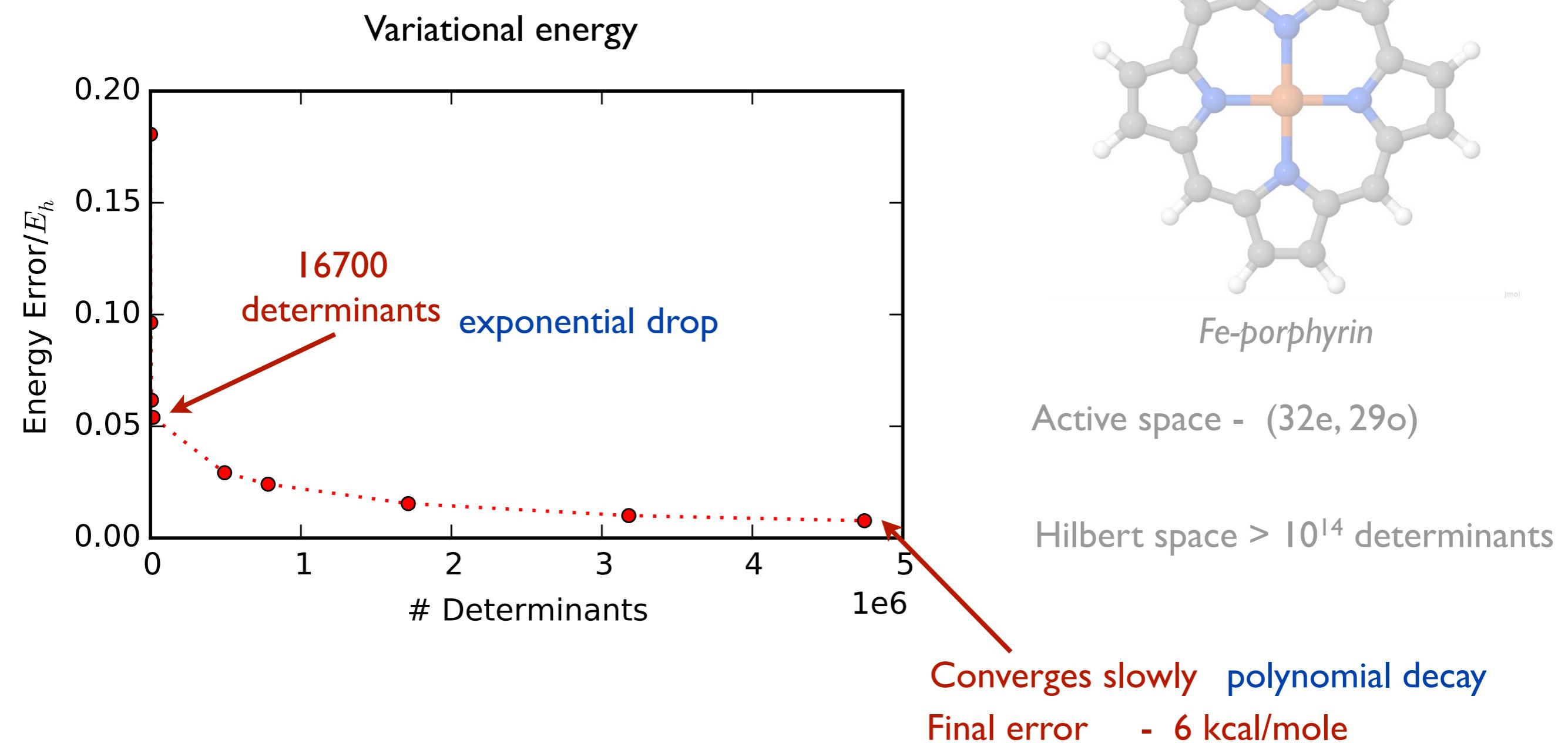
Hilbert space >  $10^{14}$  determinants

# Useful Observation

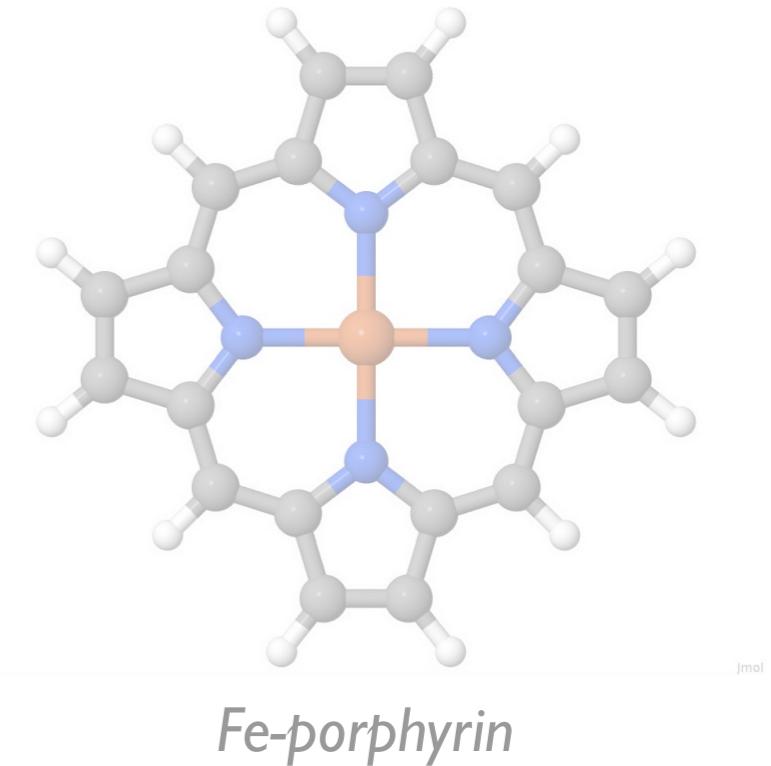
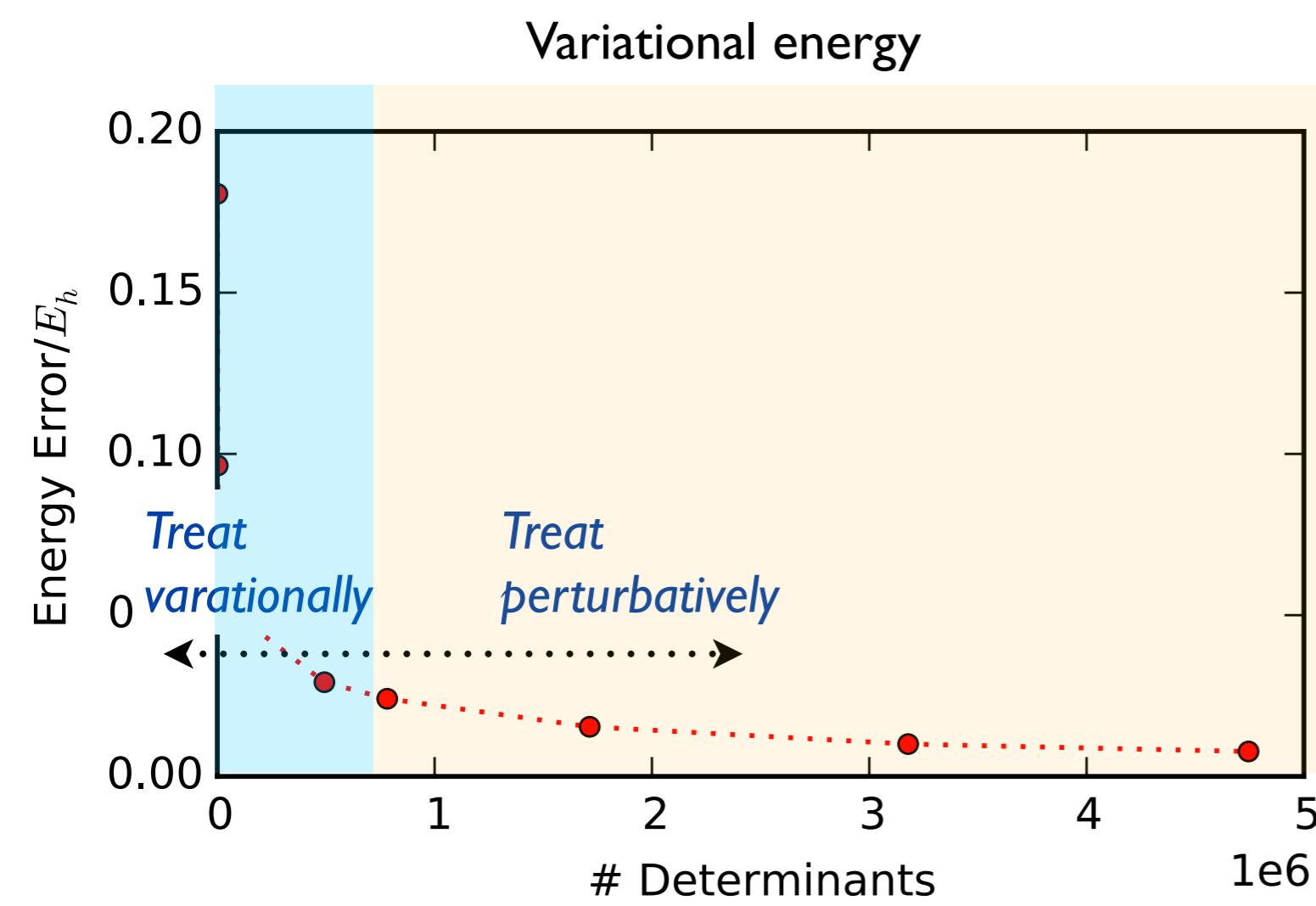


Active space - (32e, 29o)  
Hilbert space >  $10^{14}$  determinants

# Useful Observation



# Basic Idea



Active space - (32e, 29o)

Hilbert space >  $10^{14}$  determinants

# Basic procedure

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

*Solve with a small set of “important” determinants upto  $\epsilon_1$*

*How to quickly select determinants*

# Basic procedure

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

*Solve with a small set of “important” determinants upto  $\epsilon_1$*

*How to quickly select determinants*

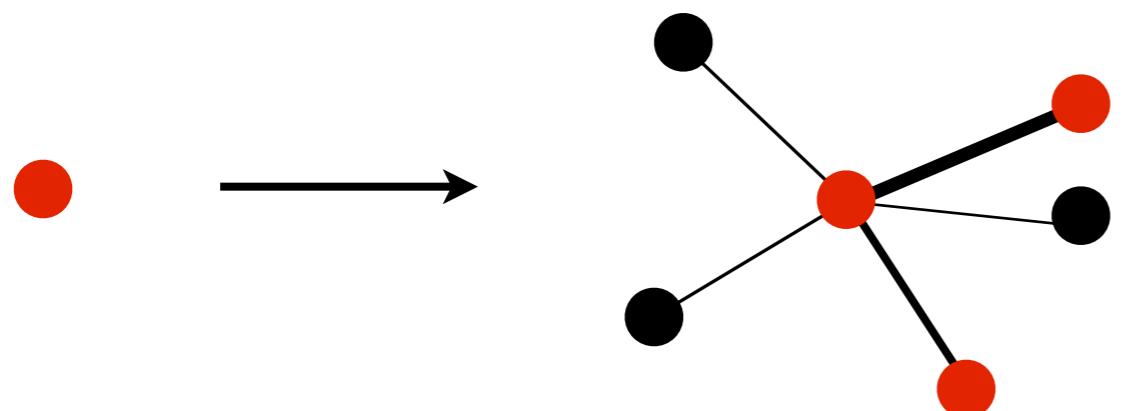


# Basic procedure

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

*Solve with a small set of “important” determinants upto  $\epsilon_1$*

*How to quickly select determinants*



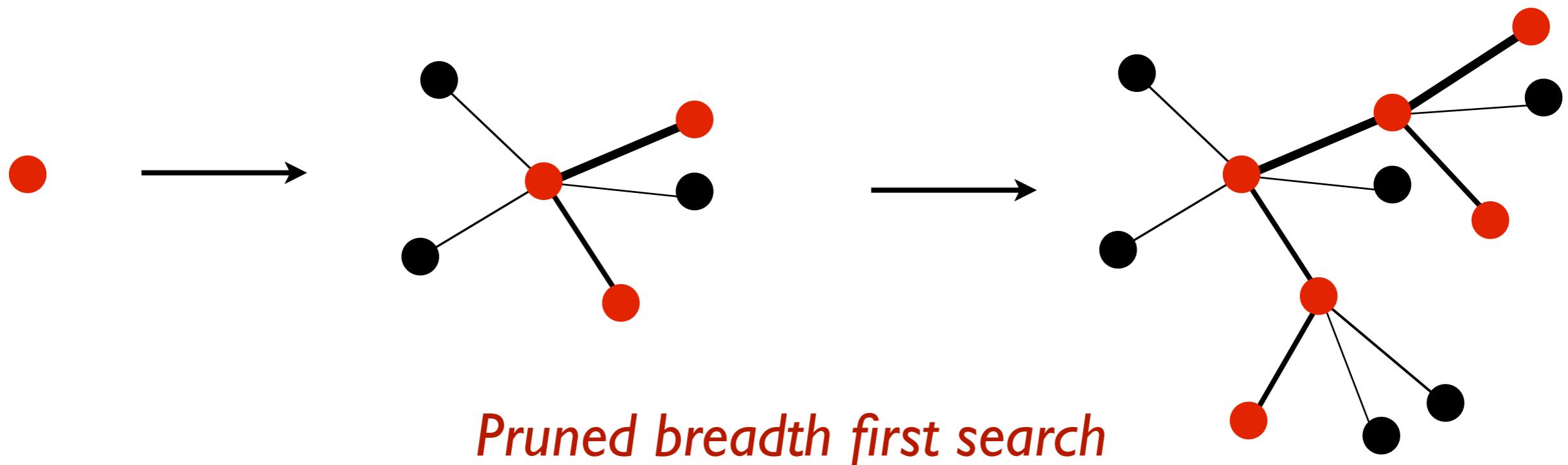
*Pruned breadth first search*

# Basic procedure

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

*Solve with a small set of “important” determinants upto  $\epsilon_1$*

*How to quickly select determinants*



# Basic procedure

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

*Solve with a small set of “important”  
determinants which  $\mathcal{E}_1$*

$$\frac{\langle D_i | V | \Psi_0 \rangle}{E_i - E_0} = \frac{\sum_j c_j H_{ij}}{E_i - E_0}$$

$$\max |c_j H_{ij}|$$



# Trick I (trivial to screen arrays that are in descending order)

$$|D_i\rangle \xrightarrow{\langle D_j | H | D_j \rangle > \epsilon} |D_j\rangle$$

# Trick I (trivial to screen arrays that are in descending order)

$$|D_i\rangle \xrightarrow{\langle D_j | H | D_j \rangle > \epsilon} |D_j\rangle$$

# Trick I (trivial to screen arrays that are in descending order)

$$\langle D_j | H | D_j \rangle > \epsilon$$
$$|D_i\rangle \xrightarrow{\hspace{1cm}} |D_j\rangle$$

electrons in orbitals  $pq$  get excited to orbitals  $rs$

$$\langle D_j | H | D_i \rangle = \langle pq || rs \rangle$$

# Trick I (trivial to screen arrays that are in descending order)

$$|D_i\rangle \xrightarrow{\langle D_j | H | D_j \rangle > \epsilon} |D_j\rangle$$

electrons in orbitals  $pq$  get excited to orbitals  $rs$

$$\langle D_j | H | D_i \rangle = \langle pq || rs \rangle$$

$$pq \rightarrow \{ \langle pq || r_1 s_1 \rangle, \langle pq || r_2 s_2 \rangle, \langle pq || r_3 s_3 \rangle, \dots \}$$

*descending order by magnitude*

*Sorting is only slightly more expensive than reading the integrals*

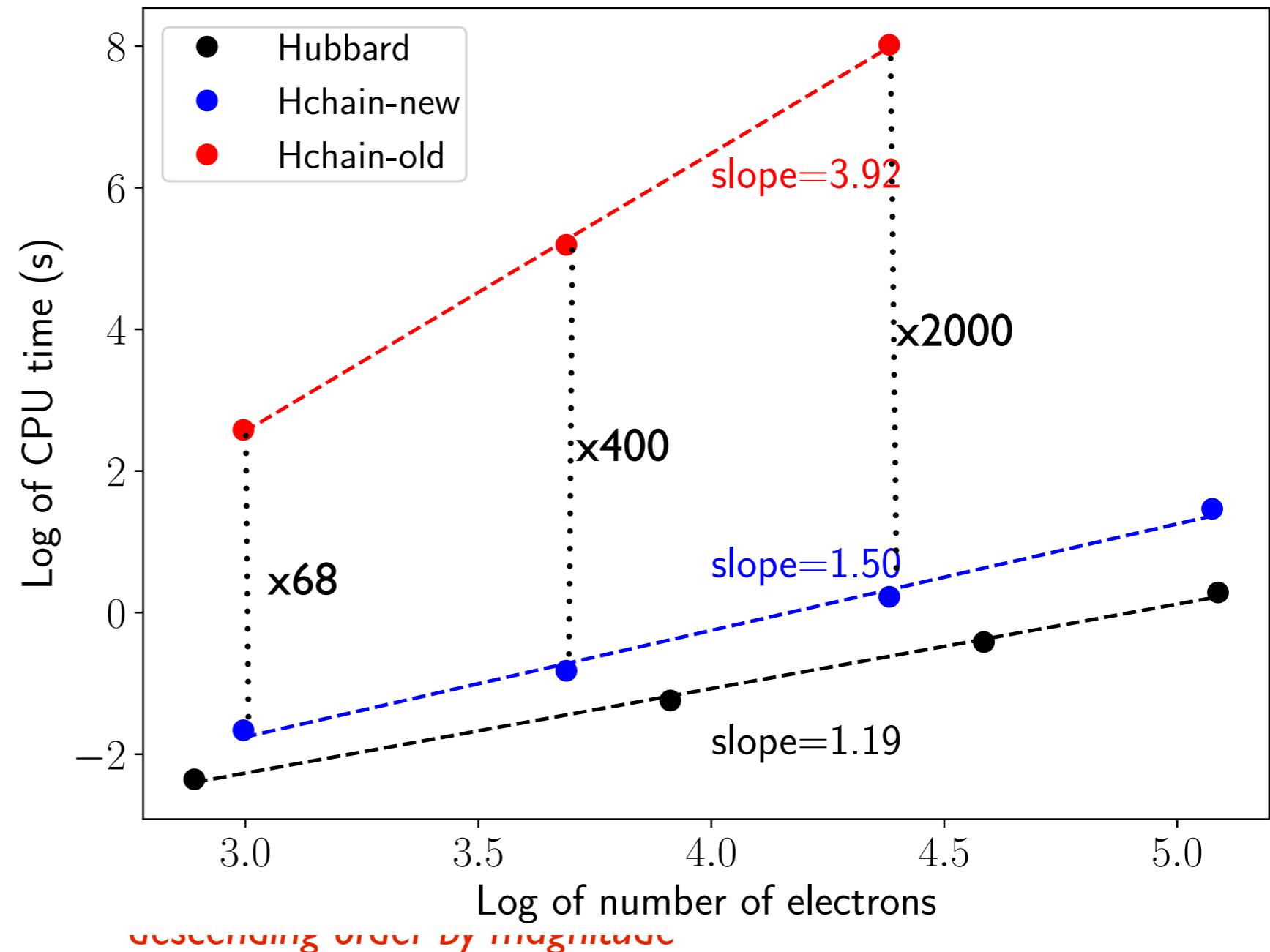
# Trick I (trivial to screen arrays that are in descending order)

Used in FCIQMC

Used in VMC

Can Even make  
Hartree Fock faster

$pq \rightarrow \{\langle x$



# Basic procedure

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

*For a small set of “important” determinants up to  $\epsilon_1$*

*How to quickly select determinants  
(we screen)*

$$(H_0 - E_0)|\Psi_1\rangle = V|\Psi_0\rangle$$

*Perform perturbative correction to the zeroth order wavefunction*

*How to overcome memory bottleneck  
(we use stochastic method)*

# Trick II (Perturbation theory can be done stochastically)

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

$$\Psi_0 | \hat{V} \frac{1}{\hat{H}_0 - E_0} \hat{V} | \Psi_0$$



sample

# Trick II (Perturbation theory can be done stochastically)

$$E = \langle \text{Tr}_+ | \hat{V} | \text{Tr}_+ \rangle^{-1} \langle \hat{V} | \text{Tr}_+ \rangle$$

Used in FCIQMC

Used in DMRG

Can be used to correct (almost) any variational calculation

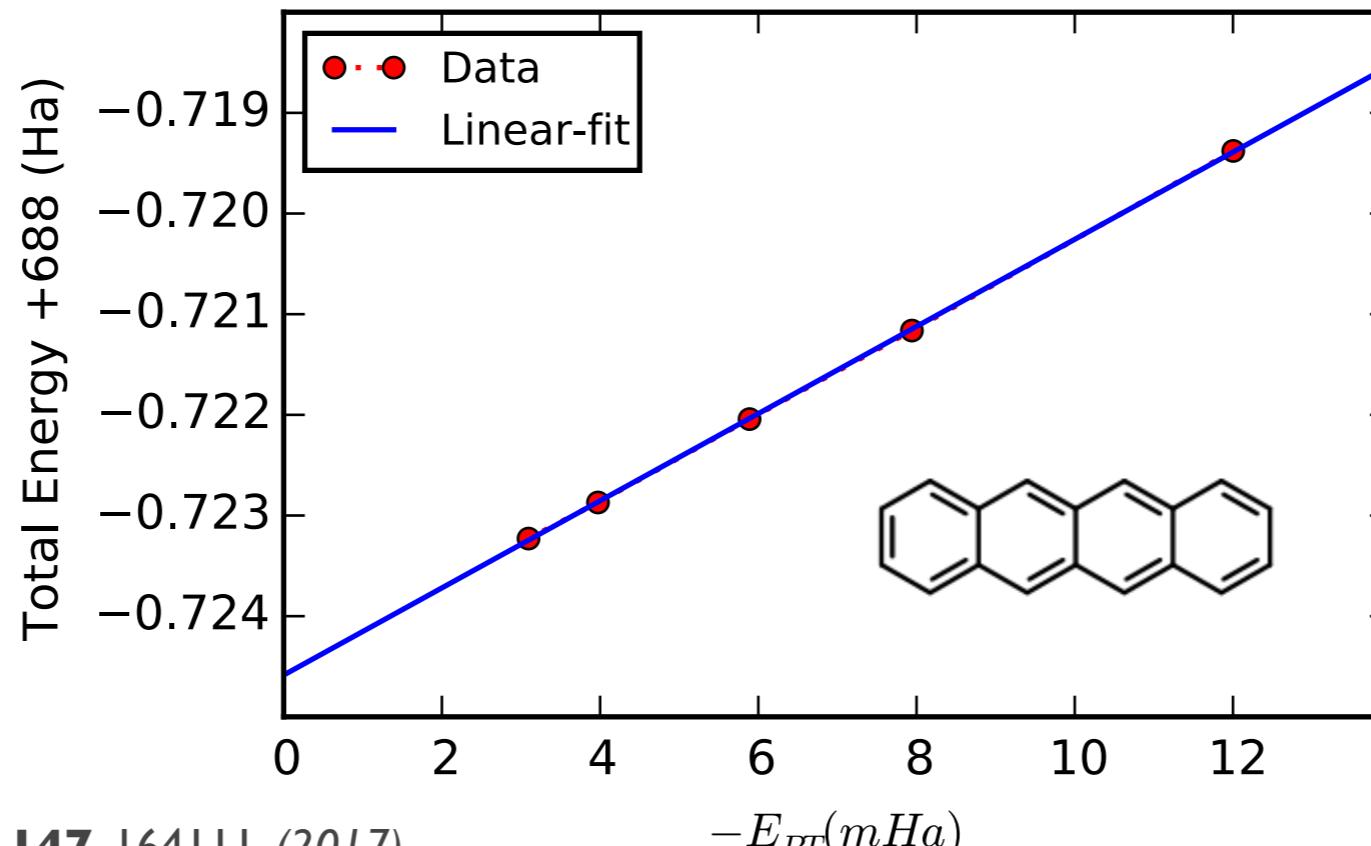
-----e

# Overall method

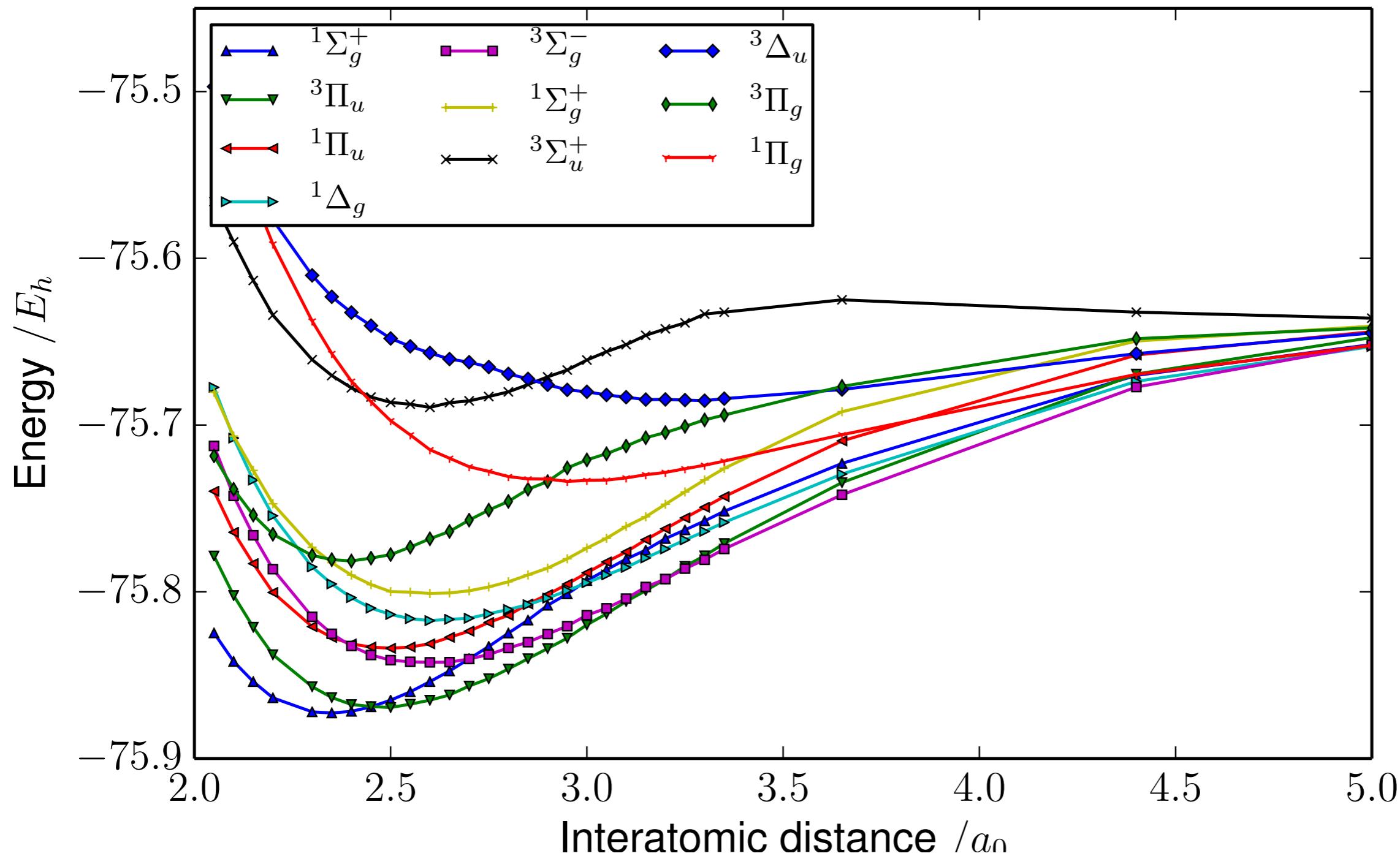
- No sign problem
- No auto-correlation length
- SHCI has only one parameter  $\epsilon_1$

# Overall method

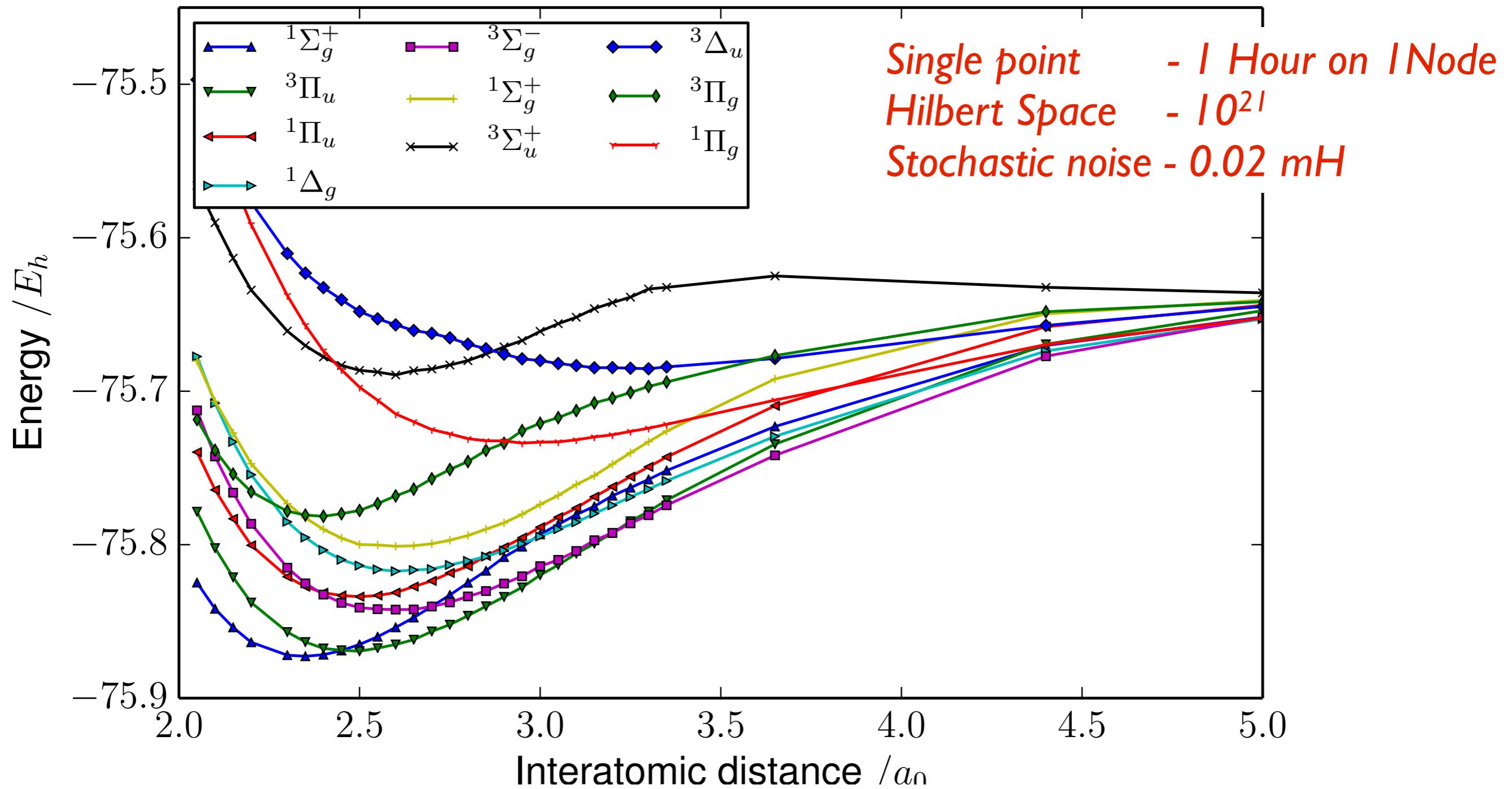
- No sign problem
- No auto-correlation length
- SHCI has only one parameter  $\epsilon_1$



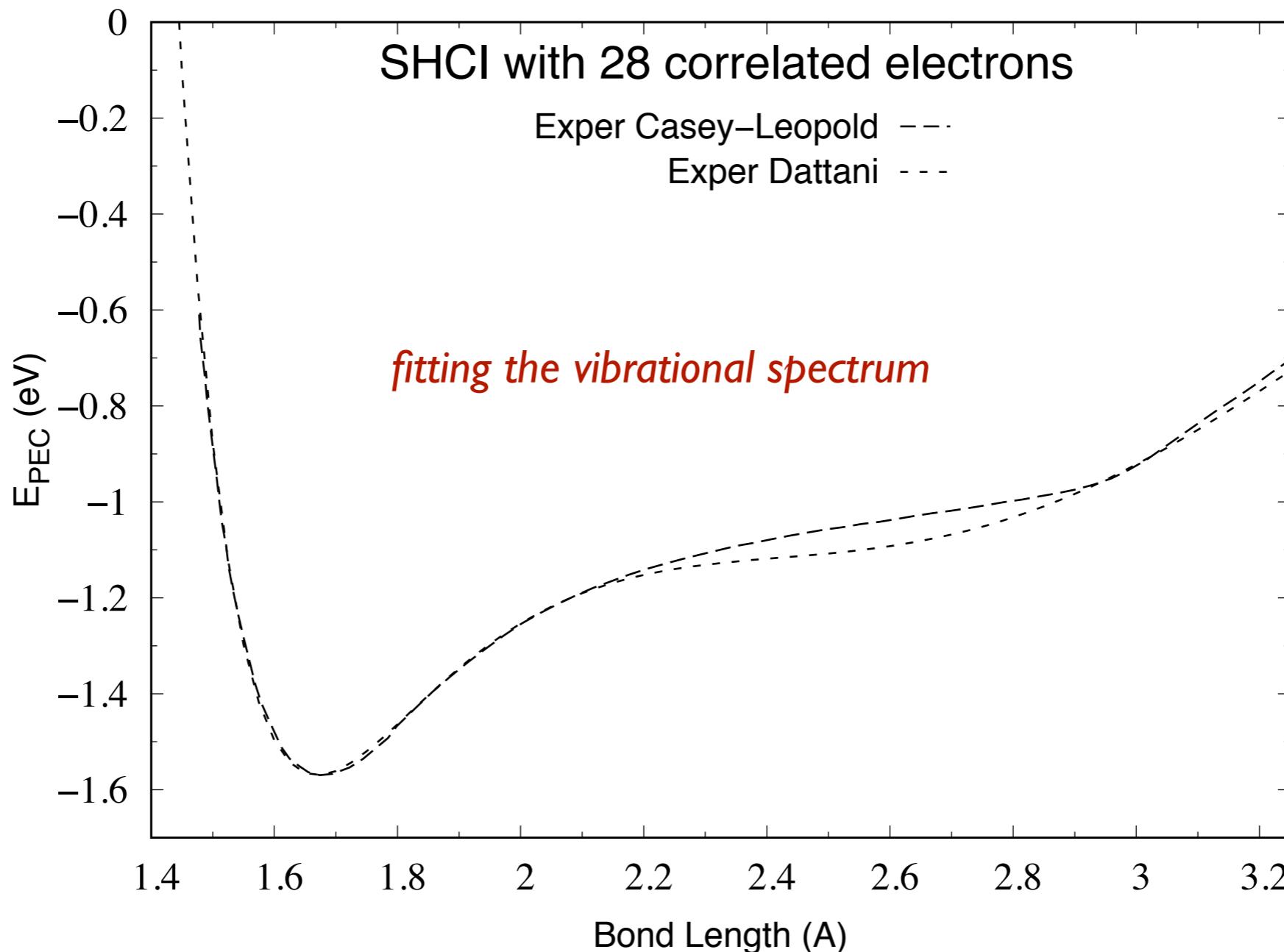
# Carbon dimer



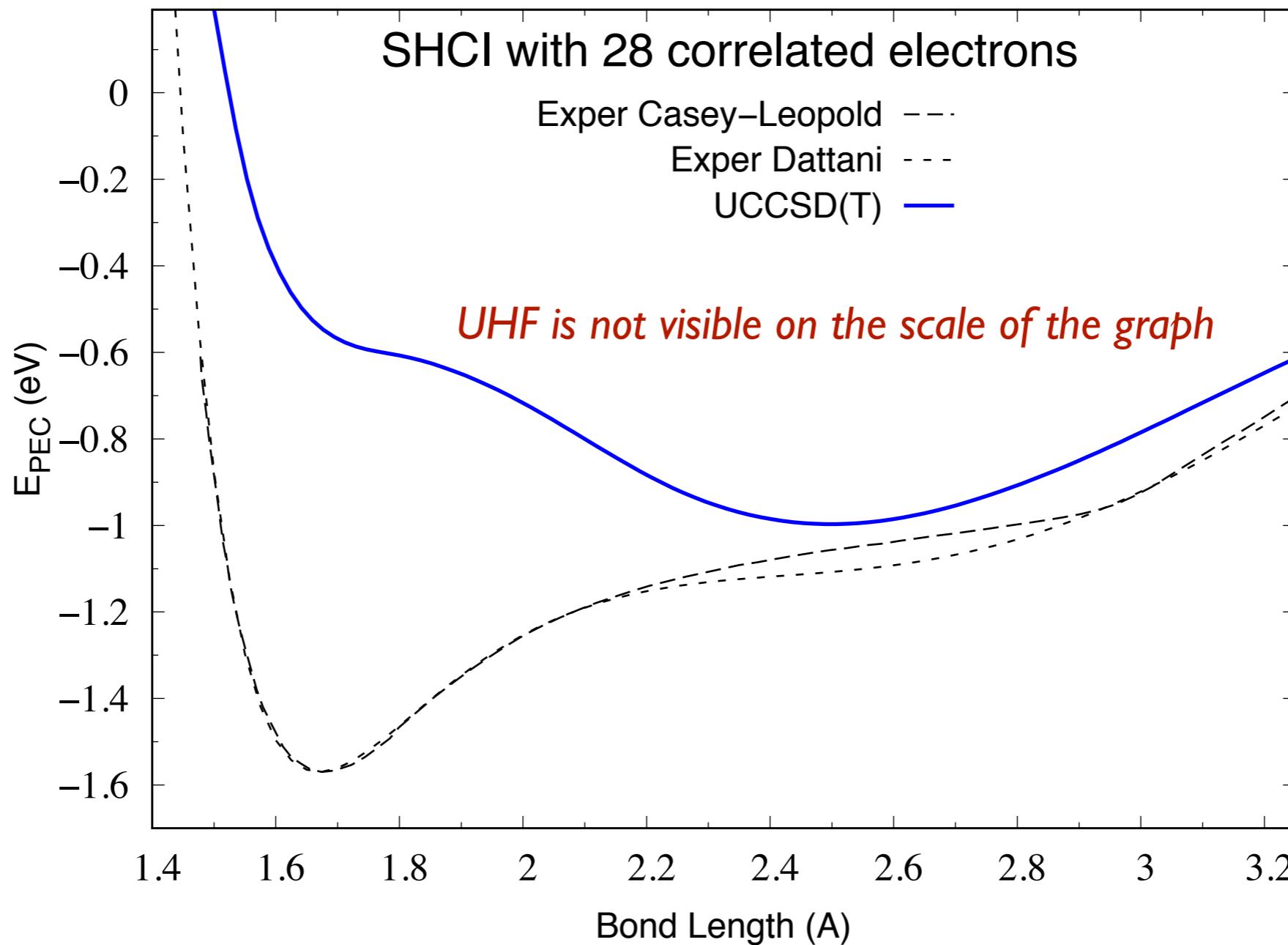
# Carbon dimer



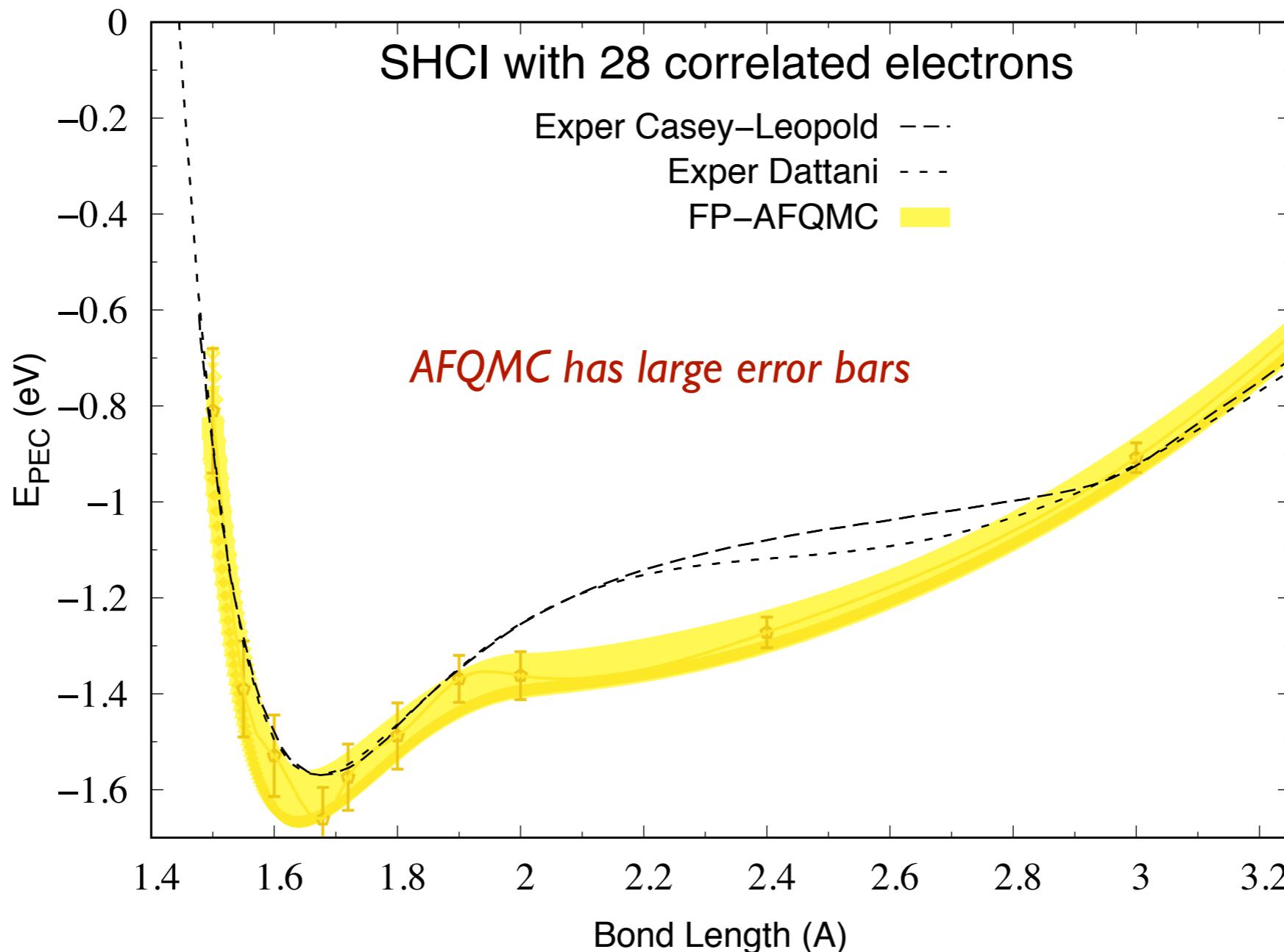
# Chromium dimer



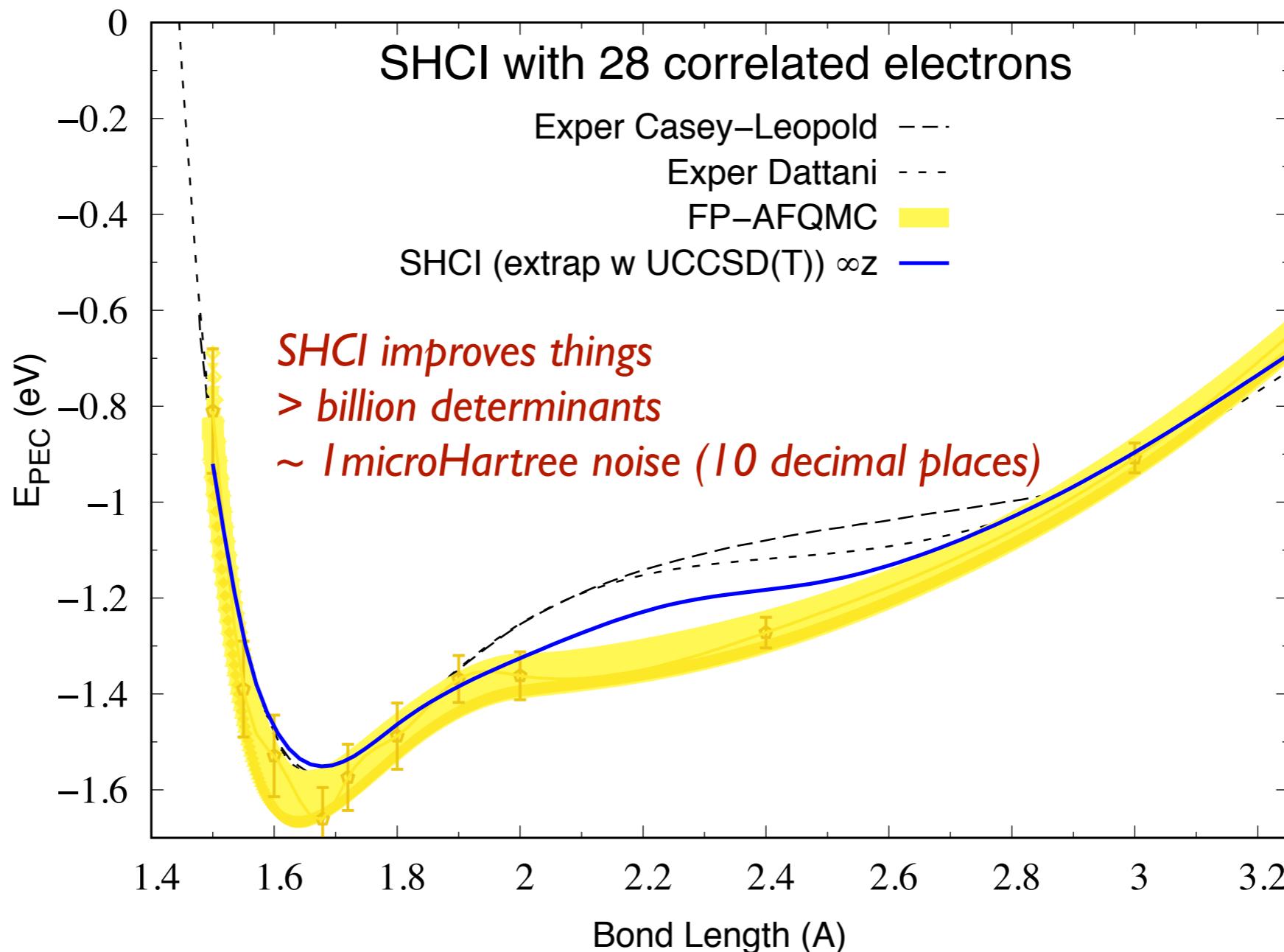
# Chromium dimer



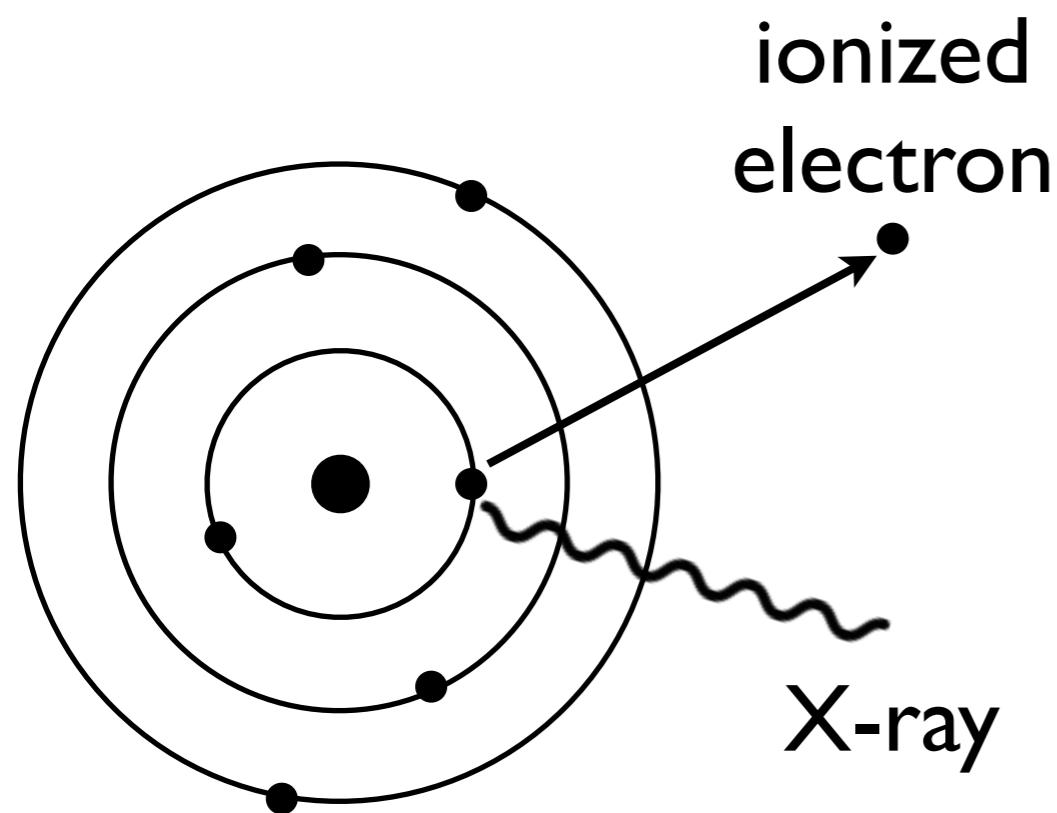
# Chromium dimer



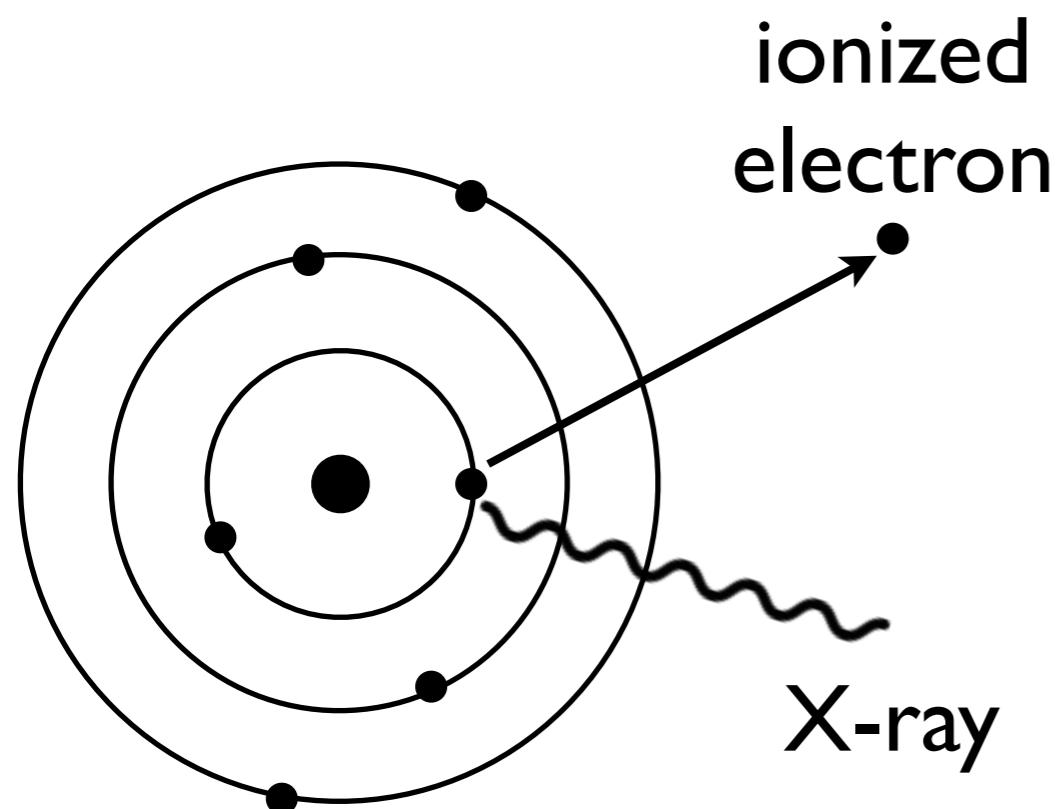
# Chromium dimer



# Core ionized states (K-edge ionization)

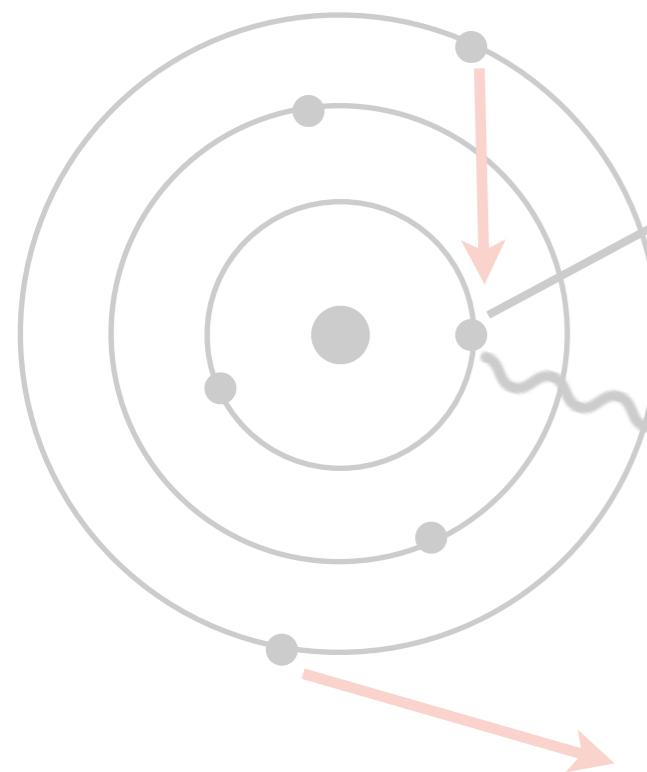


# Core ionized states (K-edge ionization)



Molecule	IP(eV)	Error
N <sub>2</sub>	410.01	0.03
CH <sub>4</sub>	291.04	0.12
HCN*	406.61	0.12
HC*N	293.60	0.11
CO*	542.43	0.08

# Core ionized states (K-edge ionization)



ionized  
electron

*The main goal is to study  
L-edge spectroscopy in transition  
metal systems*

X-ray

Molecule	IP(eV)	Error
HClN <sup>+</sup>	406.61	0.03
HC*N	293.60	0.12
CO*	542.43	0.11

*These are resonance states and we are working towards calculating lifetimes.*

# Relativistic Hamiltonian

$$\sum_i \hat{h}_D(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i,j) + V_{NN}$$

# Relativistic Hamiltonian

$$\sum_i \hat{h}_D(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + V_{NN}$$

**4-components**

$$\hat{h}_D(i) = c^2(\beta - \mathbf{I}_4) + c(\boldsymbol{\alpha}_i \cdot \hat{\mathbf{p}}_i)$$

# Relativistic Hamiltonian

$$\sum_i \hat{h}_D(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + V_{NN}$$

**4-components**       $\hat{h}_D(i) = c^2(\beta - \mathbf{I}_4) + c(\alpha_i \cdot \hat{\mathbf{p}}_i)$

$$\hat{g}(i, j) = \underbrace{\frac{1}{r_{ij}}}_{\text{Coulomb}} - \underbrace{\frac{\alpha_i \cdot \alpha_j}{r_{ij}}}_{\text{Gaunt}} + \underbrace{\left( \frac{\alpha_i \cdot \alpha_j}{2r_{ij}} - \frac{(\alpha_i \cdot \mathbf{r}_{ij})(\alpha_j \cdot \mathbf{r}_{ij})}{2r_{ij}^3} \right)}_{\text{Breit}}$$

# Relativistic Hamiltonian

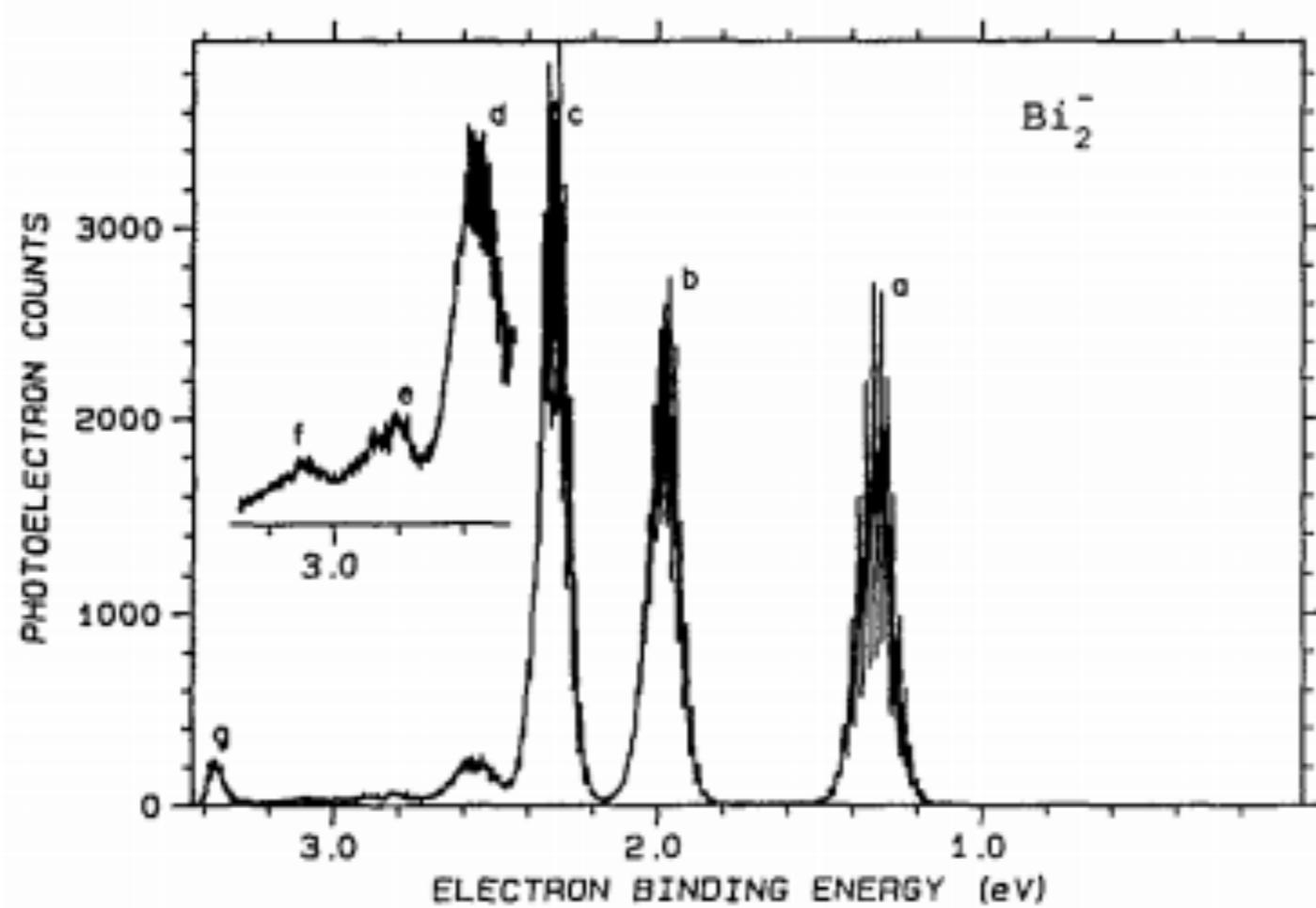
$$\sum_i \hat{h}_D(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + V_{NN}$$

- *The size of the Hilbert space of the problem sharply increases*
- *The wavefunction becomes 4-component (or 2-component quantity)*
- *Important in, phosphorescence, magnetic spectroscopy etc.*
- *Comparable to electron correlation in heavy atoms*



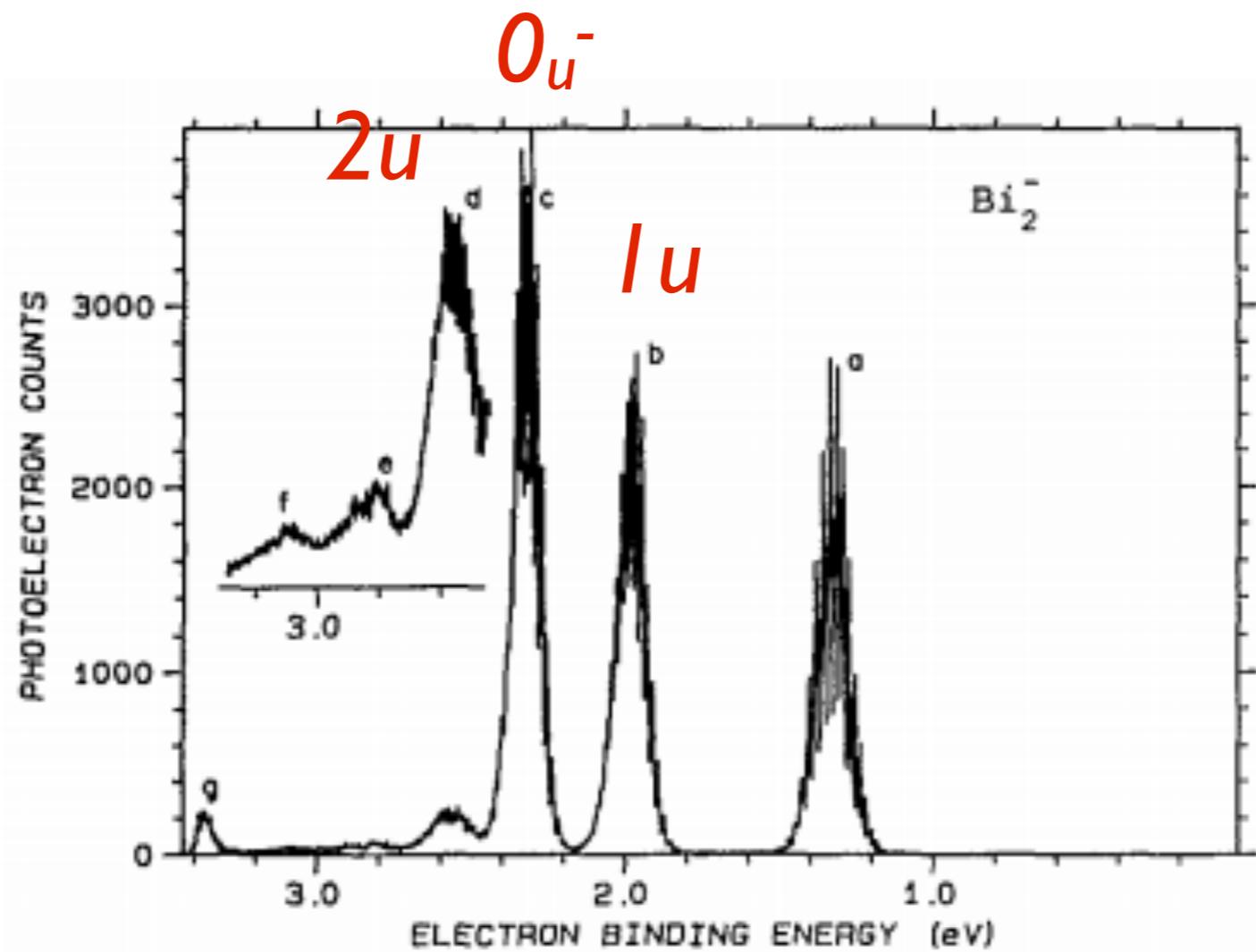
# Photoionization spectrum

$\text{Bi}_2^- \quad h\nu - eKE$

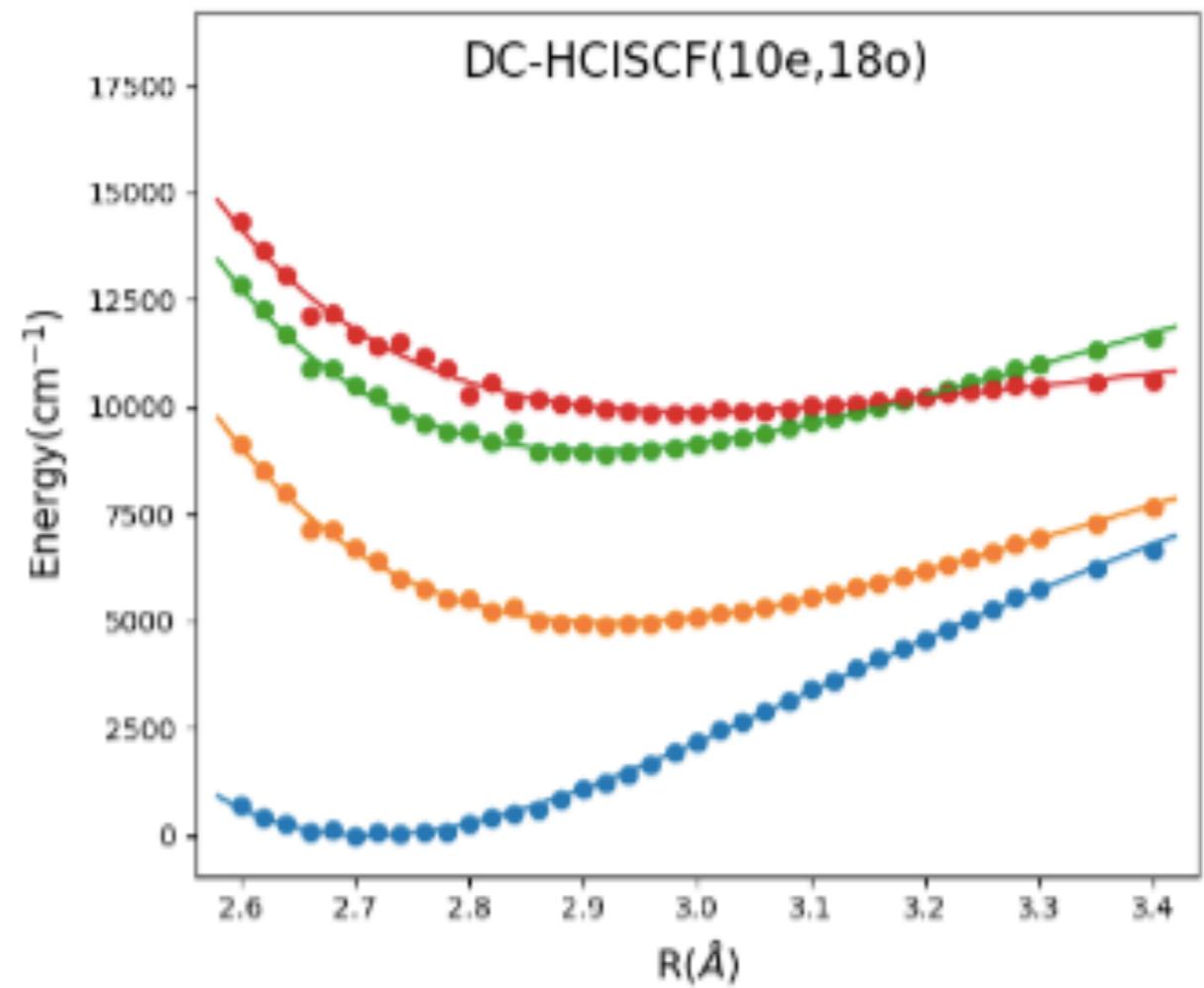
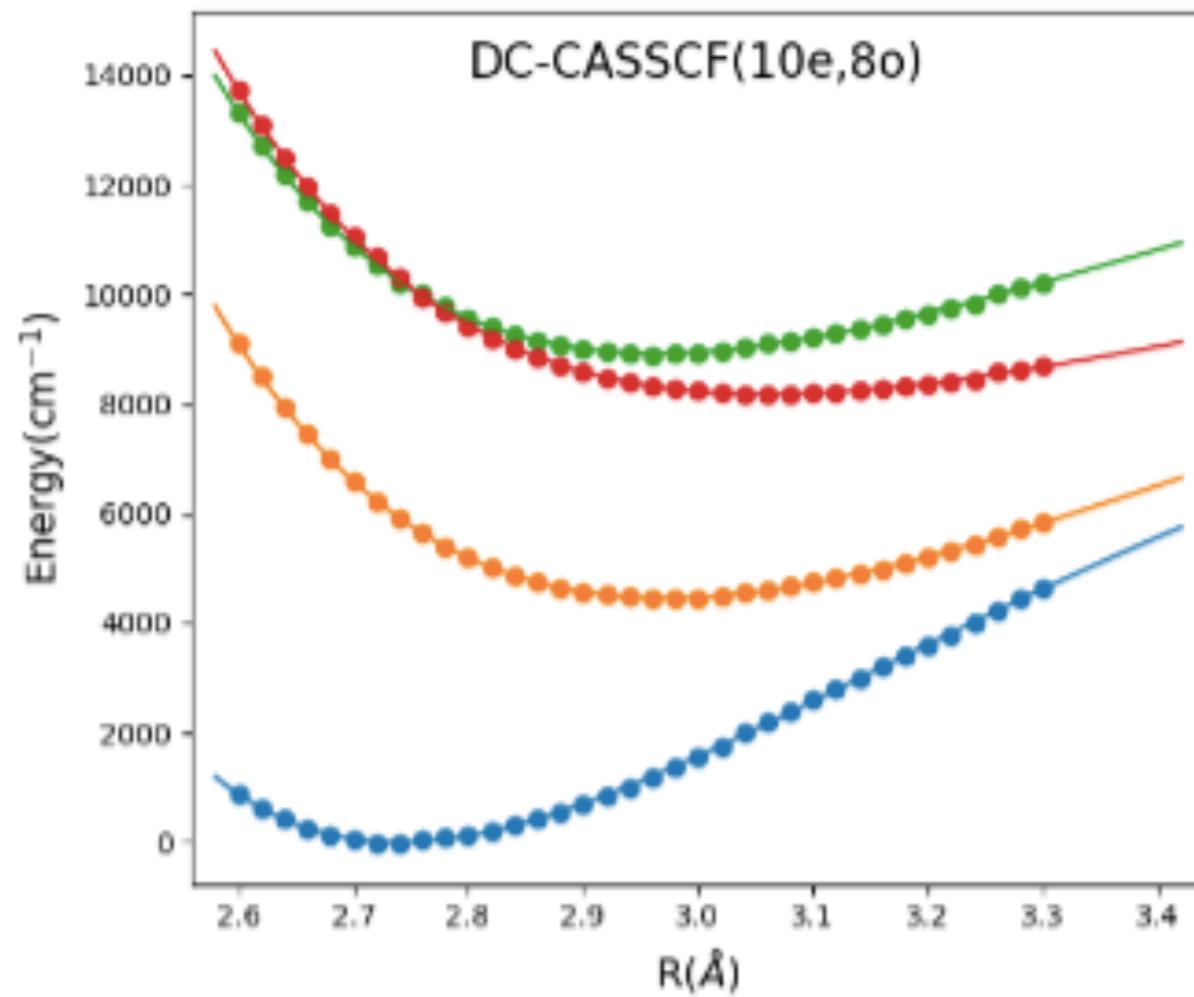


# Photoionization spectrum

$\text{Bi}_2^- \quad h\nu - eKE$

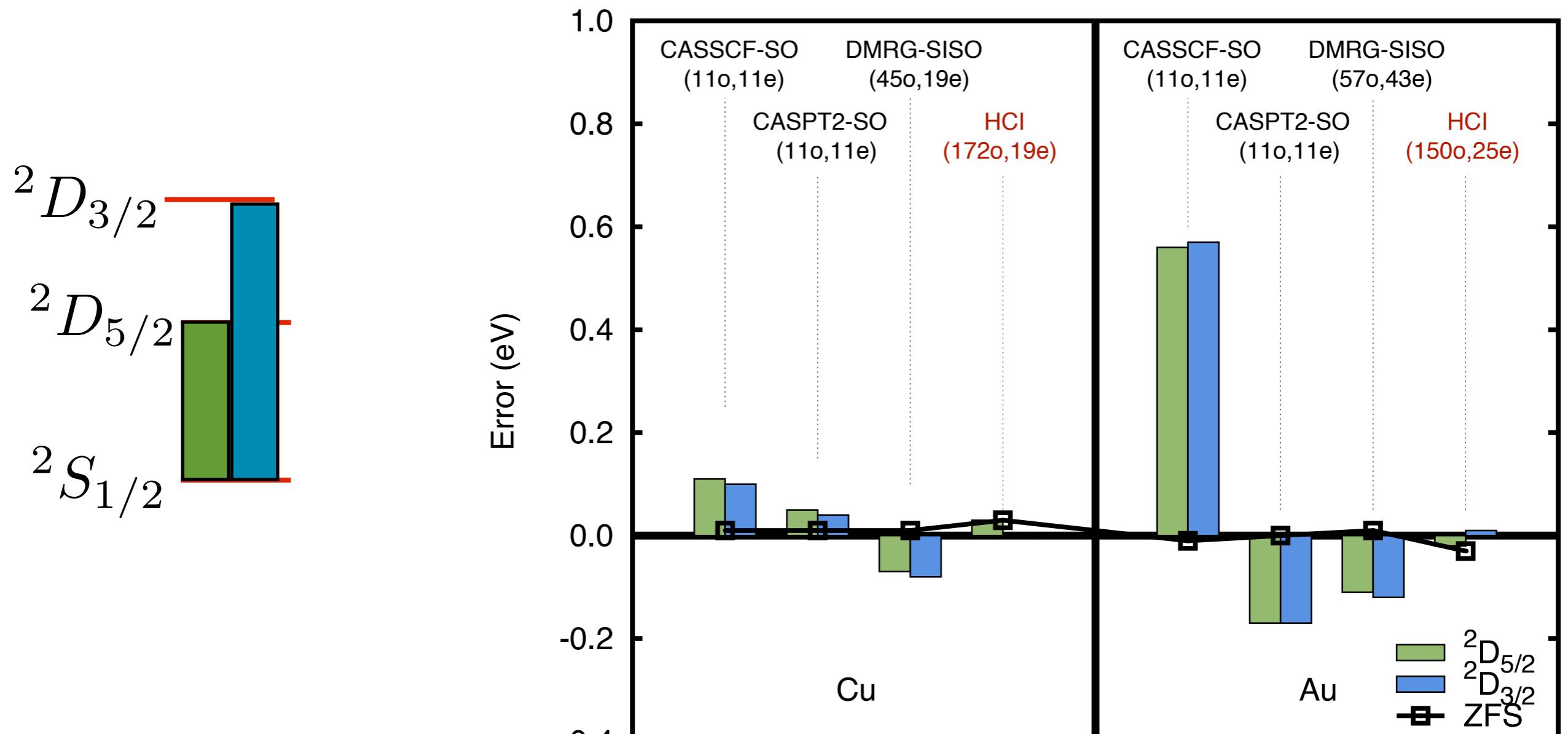


# Photoionization spectrum



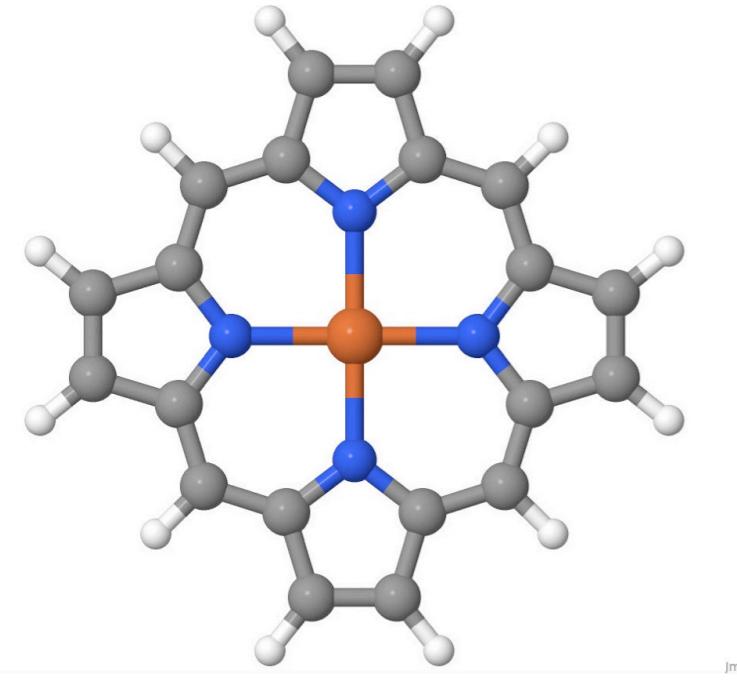
State	(10e, 8o)	(10e, 18o)	Expt
1u	4457	4967	5480
2u	8918	8969	8245
0u-	8178	9884	9900

# H + X<sub>2</sub>C (SOC) in single step (not QDPT/state-interaction)



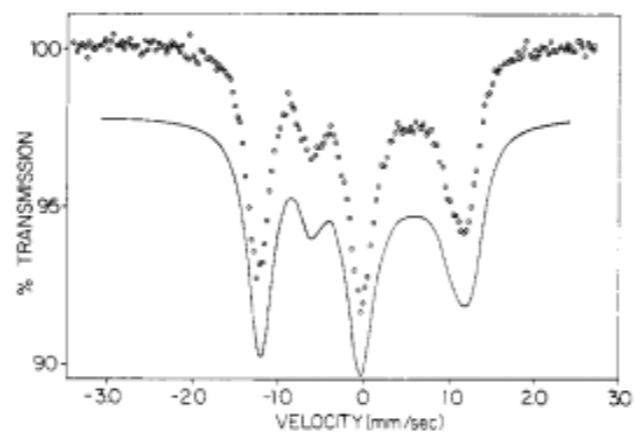
x2c scalar relativistic and SOC integrals from pyscf

# Fe-porphyrin



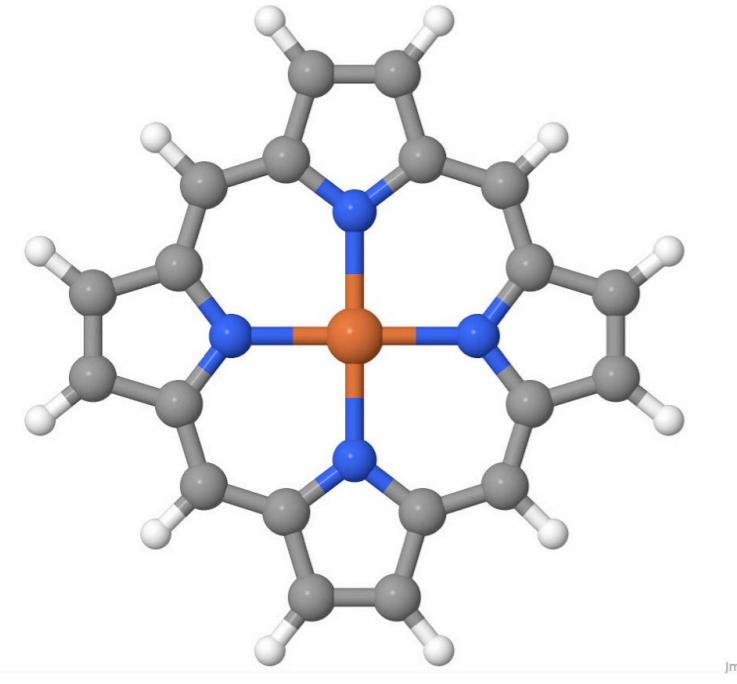
*Fe-porphyrin*

Active space - (44 e, 44o)



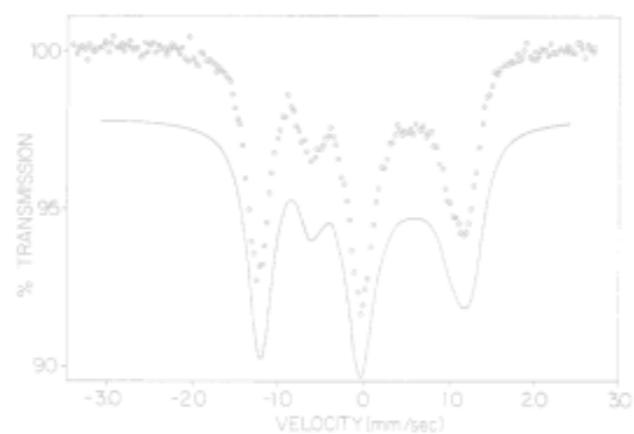
Mossbauer spectra indicates  
Fe has S=1 state  
(detects chemical shift in  
gamma-ray spectrum of nucleus)

# Fe-porphyrin



*Fe-porphyrin*

Active space - (44 e, 44o)



Mossbauer spectra indicates  
Fe has S=1 state  
(detects chemical shift in  
gamma-ray spectrum of nucleus)

*doppler shift*



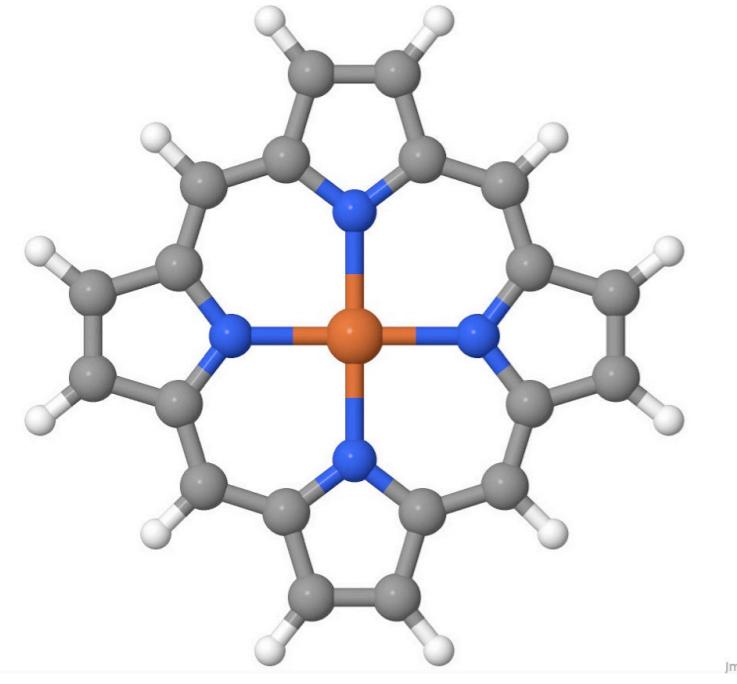
Source  
*Fe*

*Gamma rays*



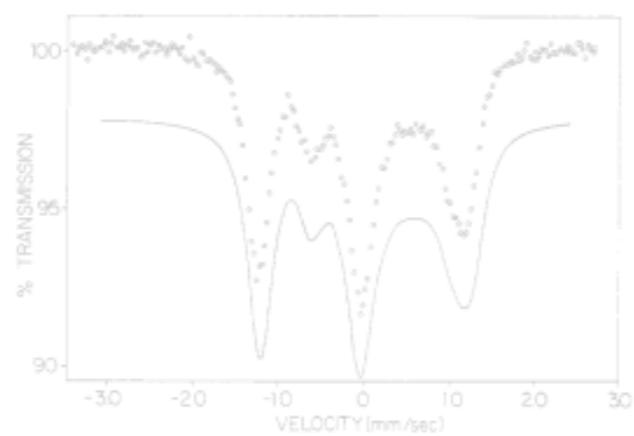
Sample  
*Fe*

# Fe-porphyrin



Fe-porphyrin

Active space - (44 e, 44o)



Mossbauer spectra indicates  
Fe has S=1 state  
(detects chemical shift in  
gamma-ray spectrum of nucleus)

doppler shift



Source  
Fe

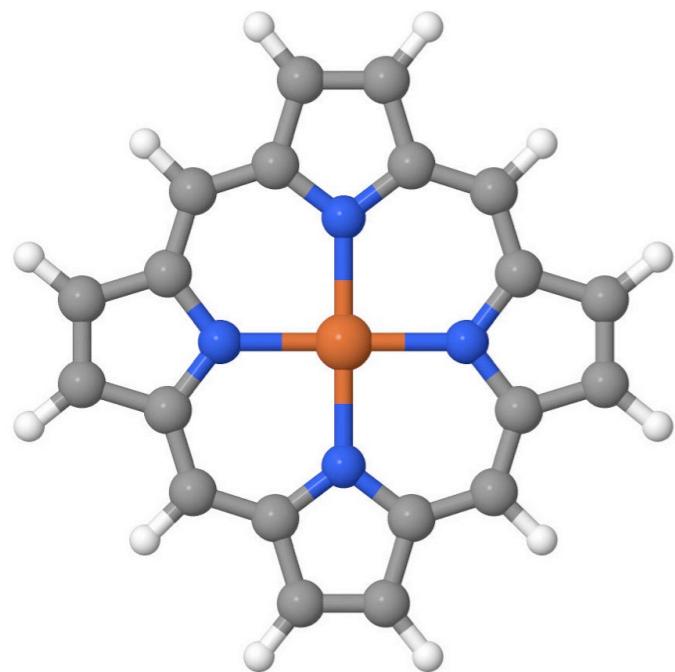


Gamma rays



Sample  
Fe

*Experimentally determined spin is S=1  
Most theoretical methods have found S=2 as the ground state*



# Fe-porphyrin

*Fe-porphyrin*

Active space - (44 e, 44o)

cc-pVDZ

$^5 A_g$

cc-pVDZ

$^3 B_{1g}$

-2244.9980

-2244.9776

CAS(29o, 32e)

-2245.0314(5)

-2245.0049(6)

wrong order

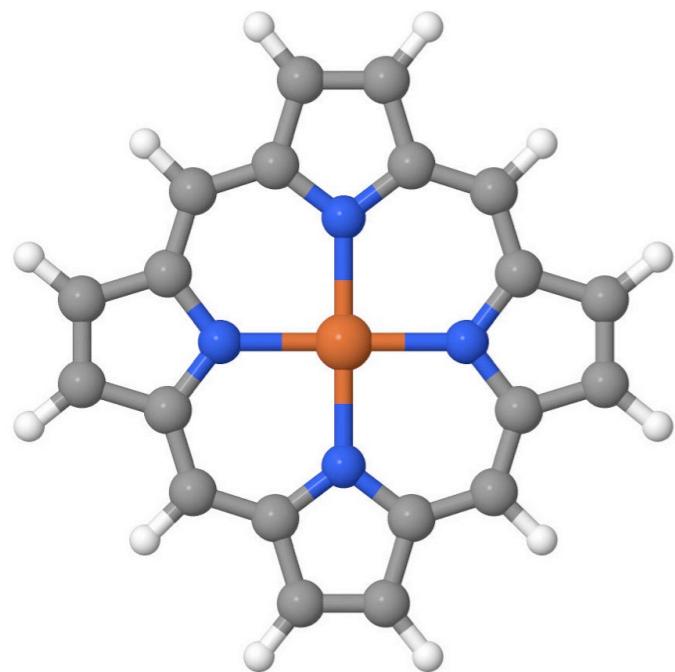
16.7

126

114

52

56

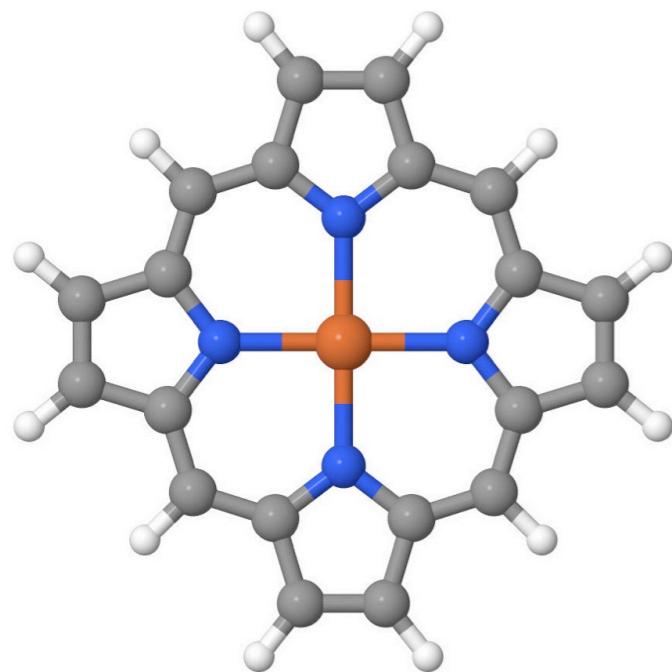


# Fe-porphyrin

*Fe-porphyrin*

Active space - (44 e, 44o)

		CAS(29o, 32e)	wrong order		
cc-pVDZ	$^5A_g$	-2244.9980	-2245.0314(5)	126	52
cc-pVDZ	$^3B_{1g}$	-2244.9776	-2245.0049(6)	114	56
cc-pVTZ	$^5A_g$	-2245.2229	-2245.2549(5)	2236	70
cc-pVTZ	$^3B_{1g}$	-2245.1958	-2245.2288(6)	2270	98



# Fe-porphyrin

*Fe-porphyrin*

Active space - (44 e, 44o)

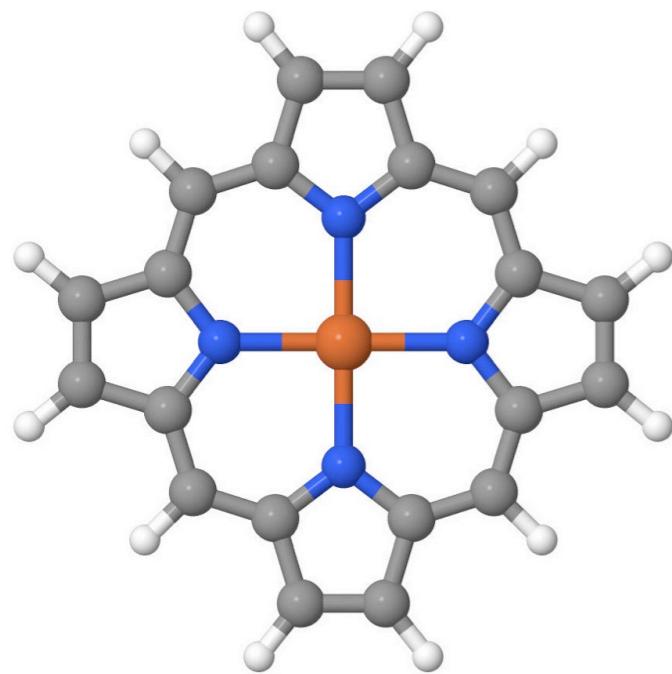
		CAS(29o, 32e)			
cc-pVDZ	$^5A_g$	-2244.9980	-2245.0314(5)	126	52
cc-pVDZ	$^3B_{1g}$	-2244.9776	-2245.0049(6)	114	56
cc-pVTZ	$^5A_g$	-2245.2229	-2245.2549(5)	2236	70
cc-pVTZ	$^3B_{1g}$	-2245.1958	-2245.2288(6)	2270	98
		CAS(44o,44e)			
cc-pVDZ	$^5A_g$	-2245.1457	-2245.1964(9)	277	185
cc-pVDZ	$^3B_{1g}$	-2245.1567	-2245.1995(6)	264	147

16.7

16.4

-2.0

*Correct order*

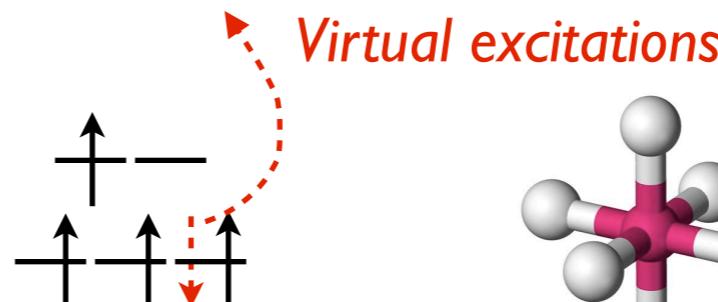


*Fe-porphyrin*

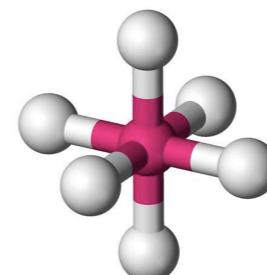
Active space - (44 e, 44o)

		CAS(29o, 32e)			
cc-pVDZ	$^5A_g$	-2244.9980	-2245.0314(5)	126	52
cc-pVDZ	$^3B_{1g}$	-2244.9776	-2245.0049(6)	114	56
cc-pVTZ	$^5A_g$	-2245.2229	-2245.2549(5)	2236	70
cc-pVTZ	$^3B_{1g}$	-2245.1958	-2245.2288(6)	2270	98
		CAS(44o,44e)			
cc-pVDZ	$^5A_g$	-2245.1457	-2245.1964(9)	277	185
cc-pVDZ	$^3B_{1g}$	-2245.1567	-2245.1995(6)	264	147

# Fe-porphyrin



low spin vs high spin



Atom with ligands

16.7

16.4

-2.0

*Correct order*

# Dynamic Correlation

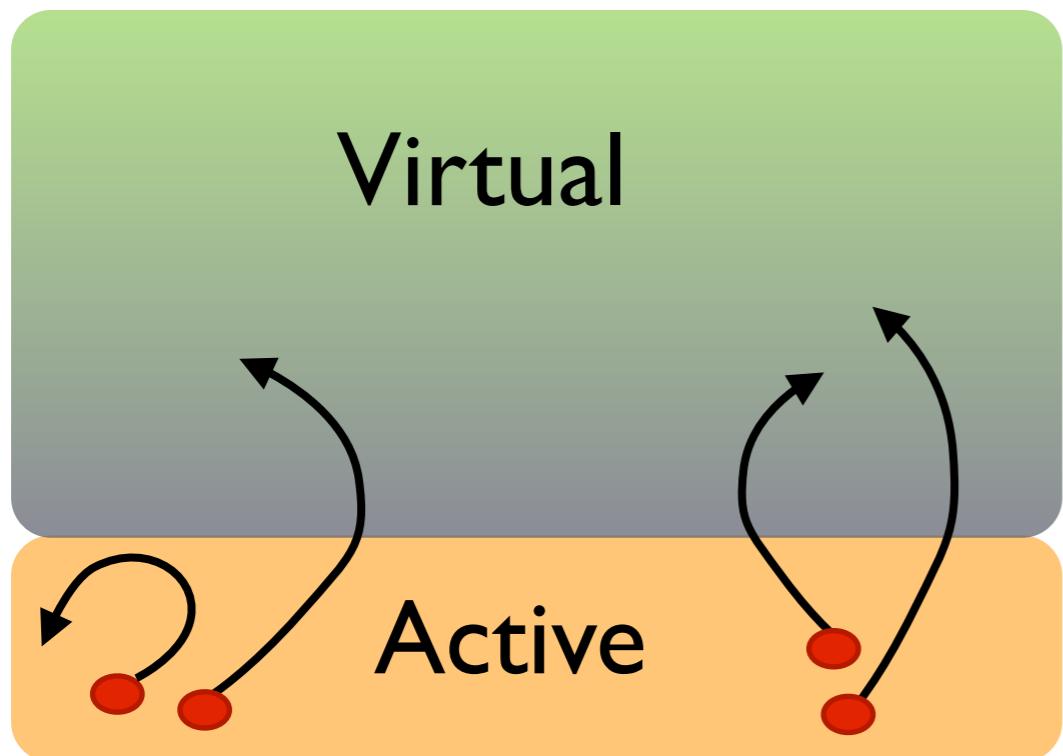


Ankit Mahajan



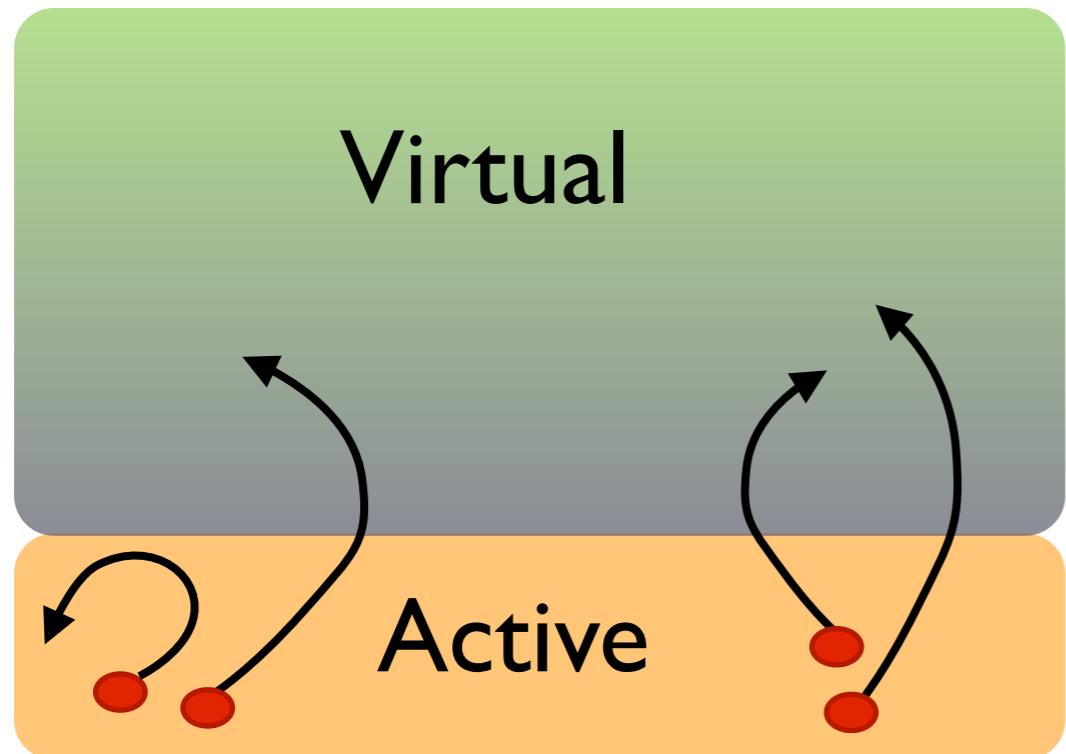
Nick Blunt

# Larger virtual spaces



SHCI runs out of steam

# Internal contraction



SHCI runs out of steam

$$\sum T_{ra}^{pq} E_{pq}^{ar} |\Psi_0\rangle \quad \sum T_{ab}^{pq} E_{pq}^{ab} |\Psi_0\rangle$$

# Perturbation theory NEVPT2

$$E^2 = \sum_l \frac{|\langle \psi_l | V | \Phi_0 \rangle|^2}{E_0 - E_l}$$

$E_l$  require up to 3 and 4 reduced density matrices

$$E_l = \frac{\langle \Psi_l | H_0 | \Psi_l \rangle}{\langle \Psi_l | \Psi_l \rangle}$$

# Internal contraction double excitation

$$H_0 \rightarrow V_{rs}^{pq} E_{pq}^{rs}$$

4 active indices

$$|\Psi_l\rangle = E_{pq}^{ab} |\Psi_0\rangle$$

2 active indices

$$E_l = \langle \Psi_l | H_0 | \Psi_l \rangle$$

8 active indices

Naive application of Wick's theorem would require 4 RDM

But  $|\Psi_0\rangle$  is an eigenfunction of  $H_0$ , only 3 RDMs required

40 orbitals  32 Gb

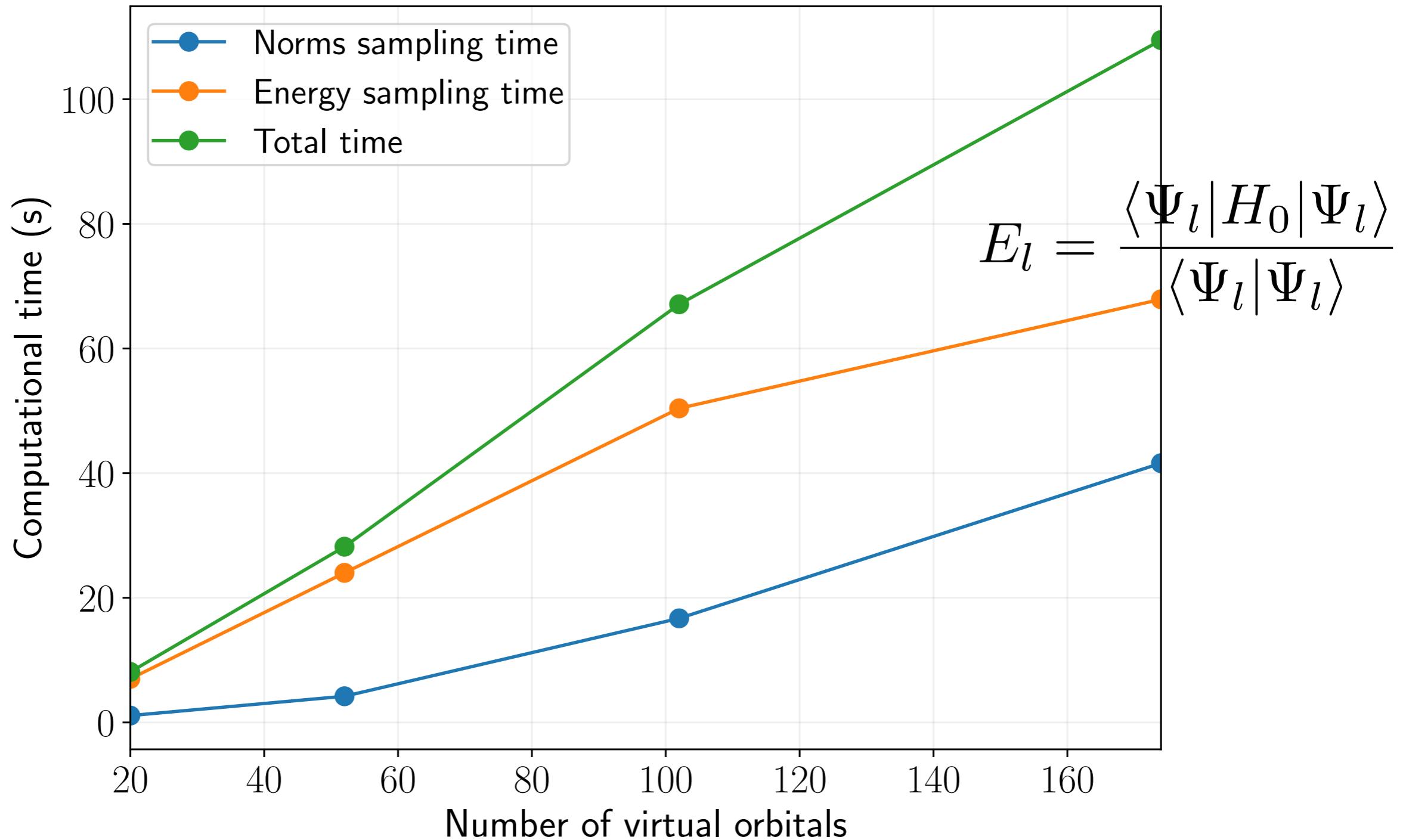
# Perturbation theory NEVPT2

$$E^2 = \sum_l \frac{|\langle \psi_l | V | \Phi_0 \rangle|^2}{E_0 - E_l}$$

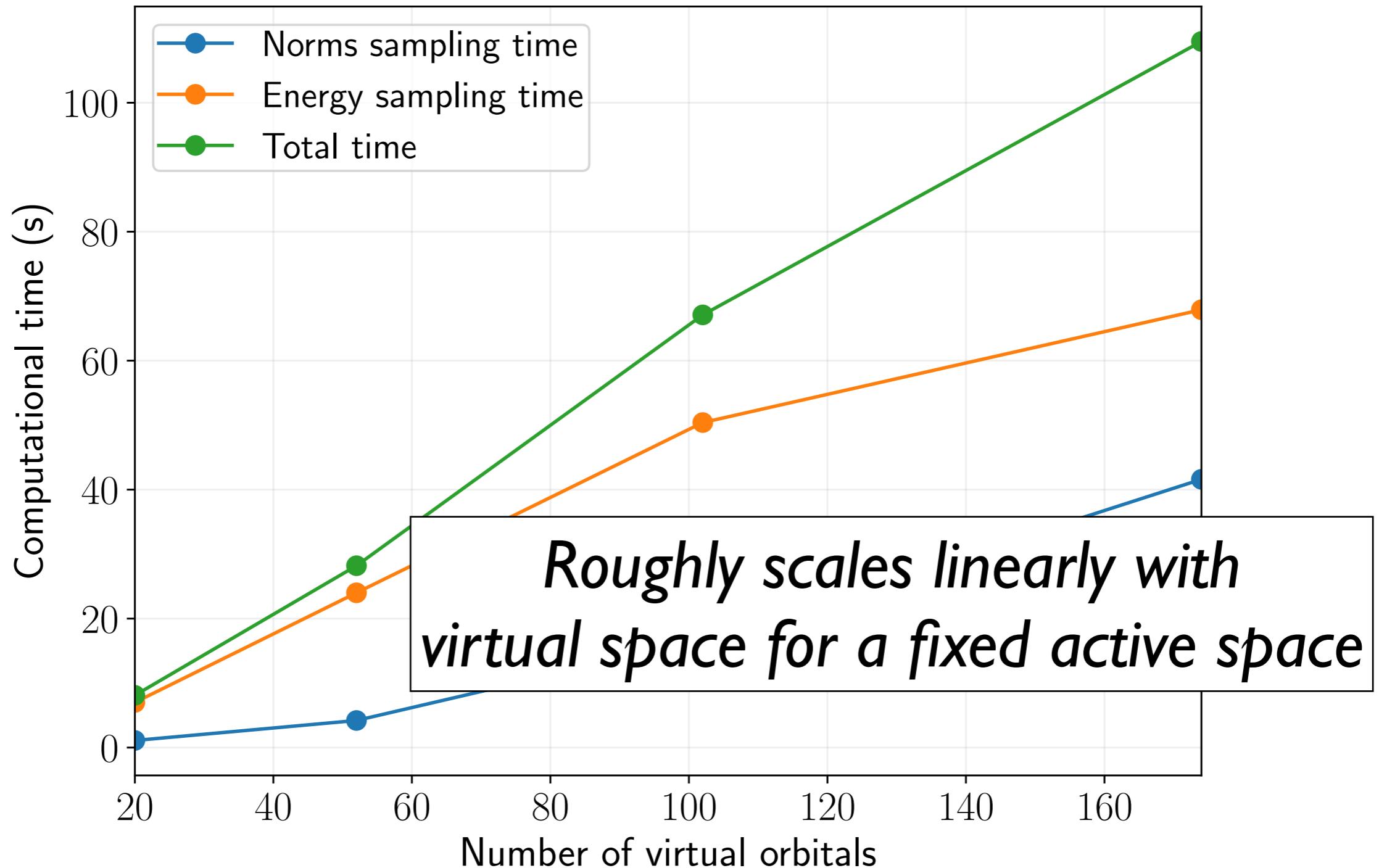
$E_l$  require up to 3 and 4 reduced density matrices

$$\begin{aligned} E_l &= \frac{\langle \Psi_l | H_0 | \Psi_l \rangle}{\langle \Psi_l | \Psi_l \rangle} \\ &= \sum_n \frac{|\langle n | \Psi_l \rangle|^2}{\langle \Psi_l | \Psi_l \rangle} \frac{\langle n | H_0 | \Psi_l \rangle}{\langle n | \Psi_l \rangle} \\ &= \langle E_L[n] \rangle_{\rho_n} \quad \rho_n \quad \rightarrow \quad E_L[n] \end{aligned}$$

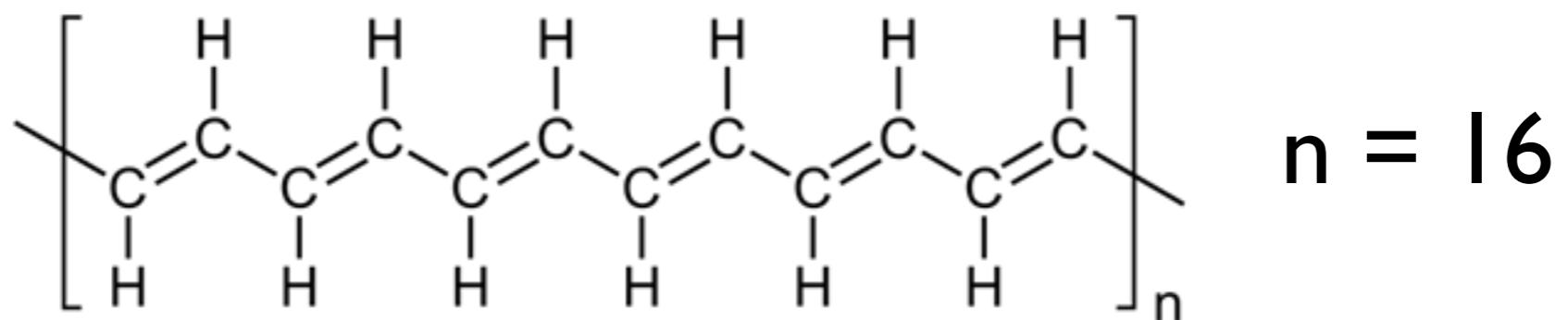
# Scaling with virtual orbitals



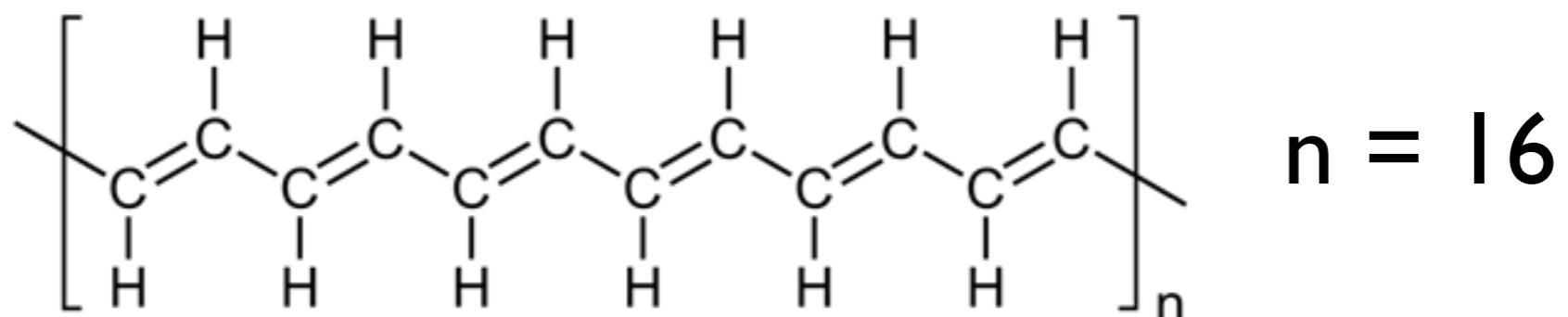
# Scaling with virtual orbitals



# Shortcoming of reference state

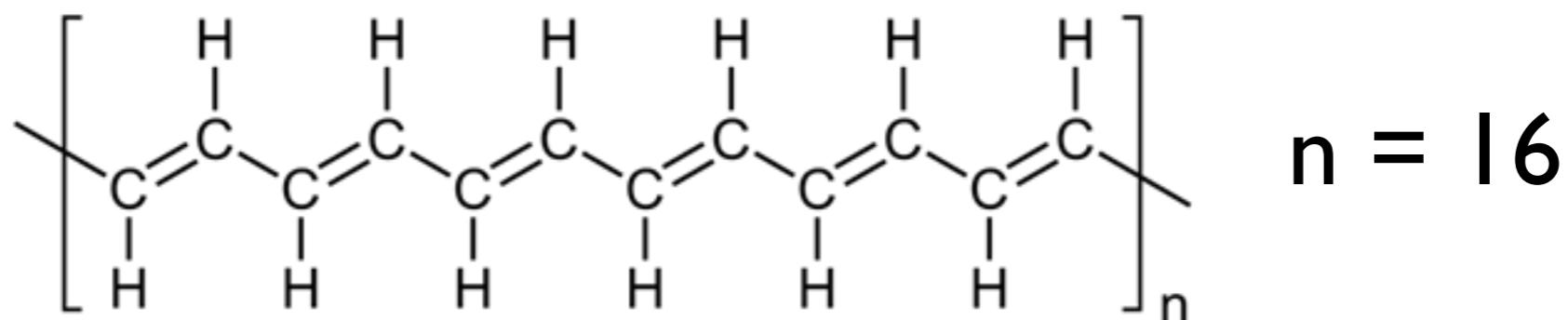


# Shortcoming of reference state



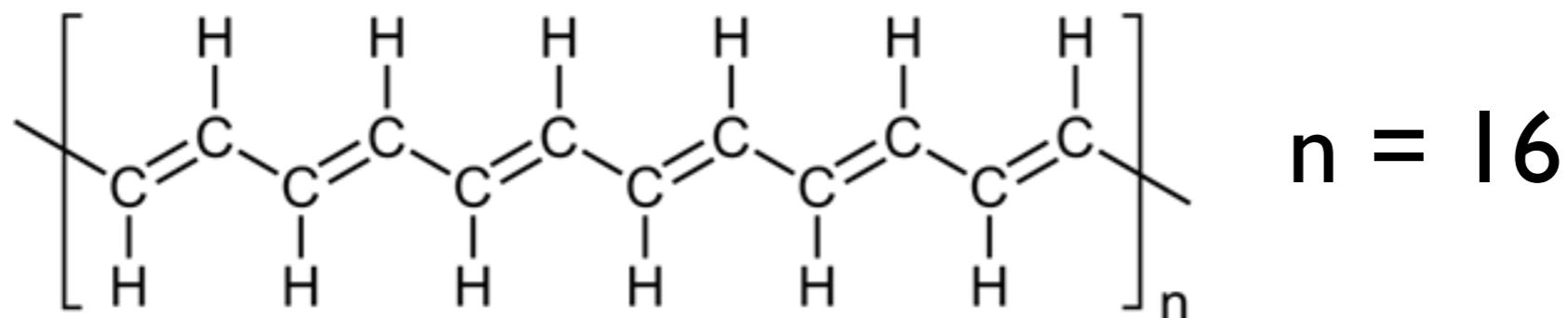
# dets	$E_0$	$E_0 + \text{NEVPT2}$
11,563	-616.206	-617.435

# Shortcoming of reference state



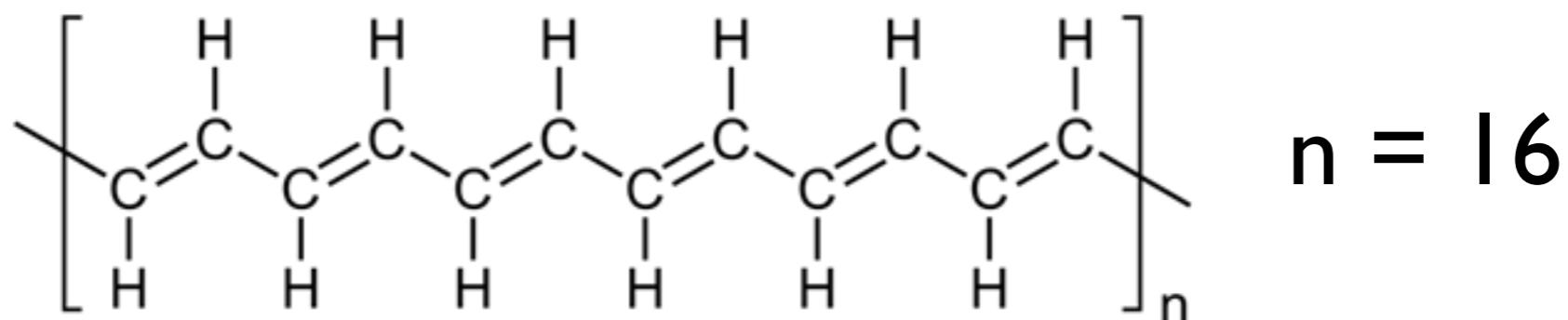
# dets	$E_0$	$E_0 + \text{NEVPT2}$
11,563	-616.206	-617.435
235,090	-616.234	-617.438

# Shortcoming of reference state



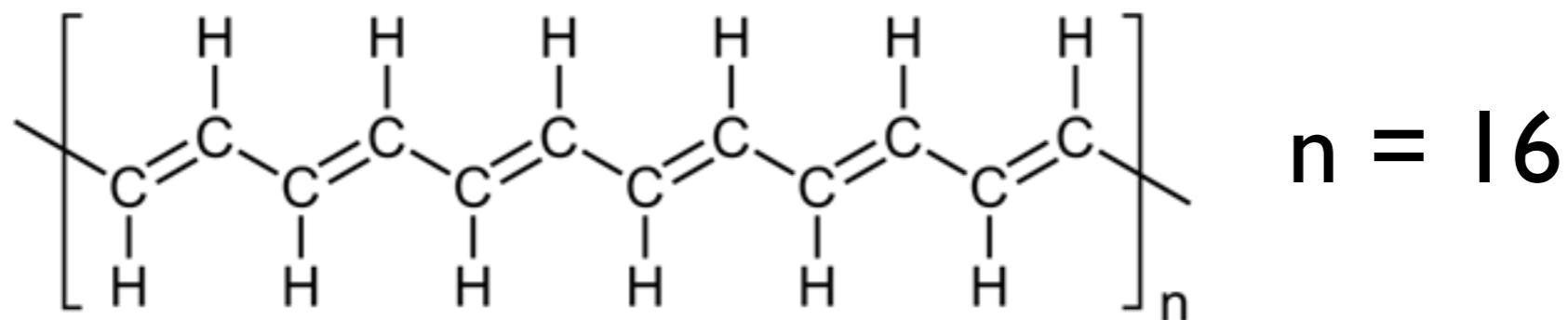
# dets	$E_0$	$E_0 + \text{NEVPT2}$
11,563	-616.206	-617.435
235,090	-616.234	-617.438
626,661	-616.239	-617.438

# Shortcoming of reference state



# dets	$E_0$	$E_0 + \text{NEVPT2}$
11,563	-616.206	-617.435
235,090	-616.234	-617.438
626,661	-616.239	-617.438
6,414,554	-616.243	-617.438

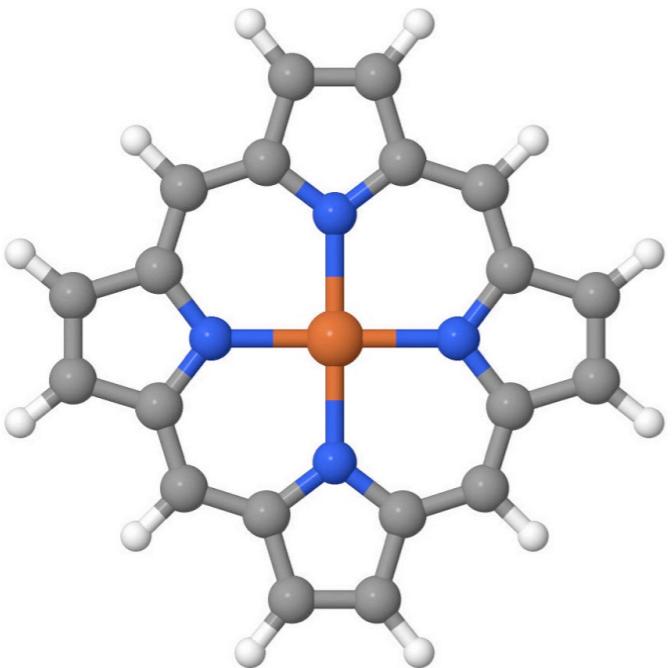
# Shortcoming of reference state



# dets	$E_0$	$E_0 + \text{NEVPT2}$
11,563	-616.206	-617.435
235,090	-616.234	-617.438
626,661	-616.239	-617.438
6,414,554	-616.243	-617.438

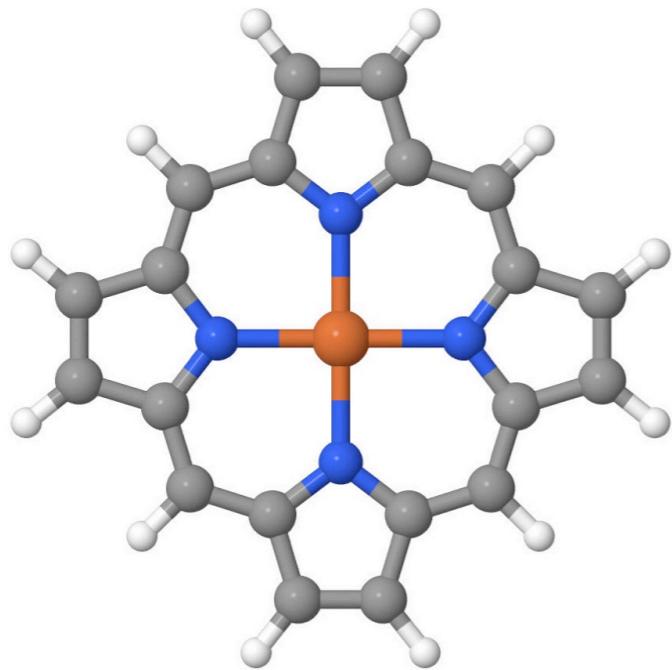
Scaling with active space  $\sim n^8$  (probably can reduce to  $n^5$ )

# Sampling efficiency



44 core  
(32e, 29o)  
~330 virtuals  
(DZ basis)

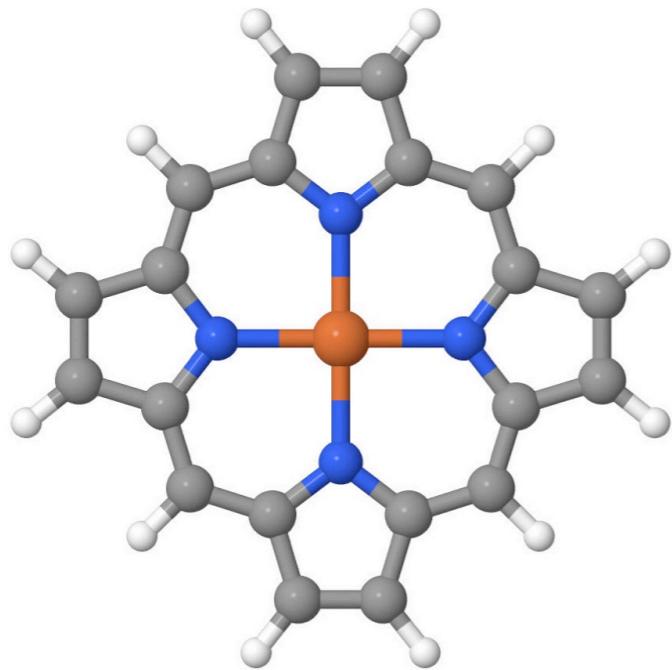
# Sampling efficiency



44 core  
(32e, 29o)  
~330 virtuals  
(DZ basis)

*Sampling efficiency*  
 $10^7$  out of  $10^{12}$  determinants visited

# Sampling efficiency



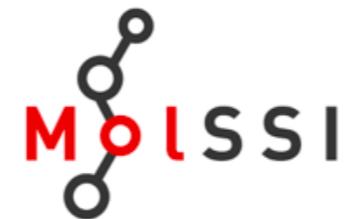
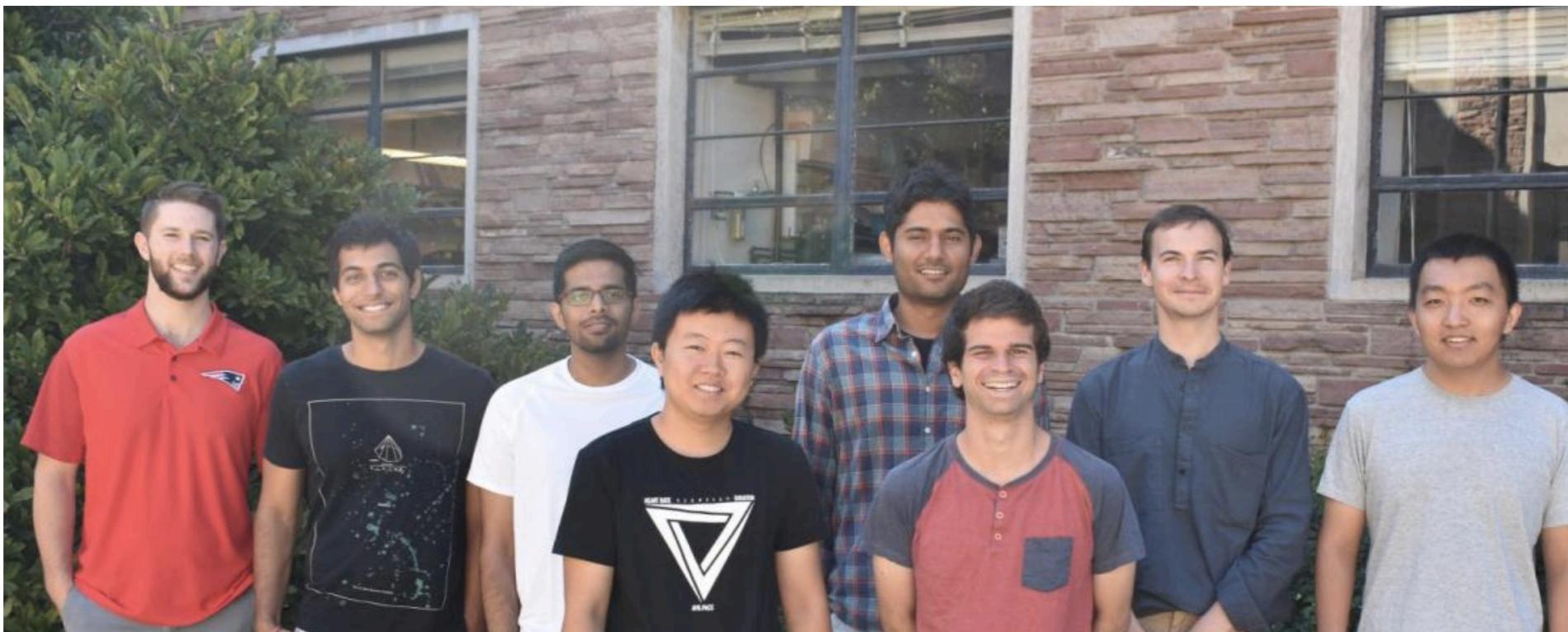
44 core  
(32e, 29o)  
~330 virtuals  
(DZ basis)

*Sampling efficiency*  
 $10^7$  out of  $10^{12}$  determinants visited

*CPU cost*

20 hrs - 1 node  
5 hrs - 4 node

# Acknowledgements



Thanks for your  
patience and happy to  
answer any questions