A pedagogical introduction to the "SHCI" algorithm.

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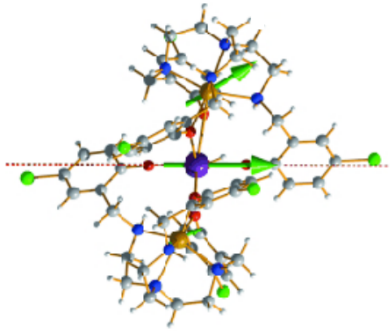
Spin-orbit coupling

X. Wang, B.Mussard

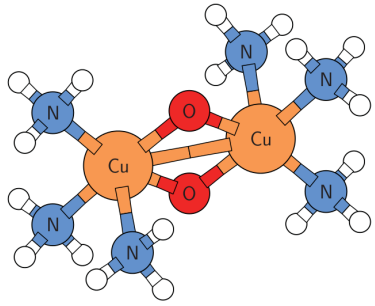
- Four-component DCB Hamiltonian exactly;
- Ab-initio parameters for model spin-Hamiltonian (analytical response theory).



Multireference perturbation theory

B. Mussard

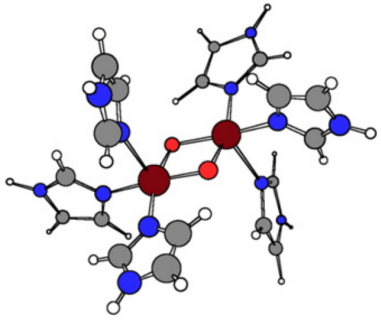
- Calculations of Cupper oxides;
- Use of ML techniques that would forego the need of RDMs altogether.



Embedding techniques

J.E.T. Smith, B. Mussard

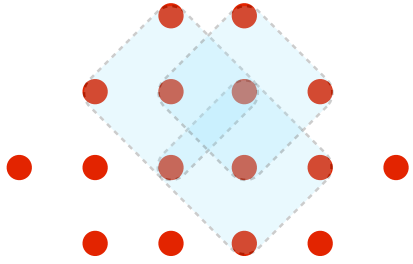
- Use projection-based embedding to tackle large systems of interest.



Orbital space VMC

I. Sabzevari, A. Mahajan

- Use of ML minimizer to optimize large numbers of parameters of a flexible wft;

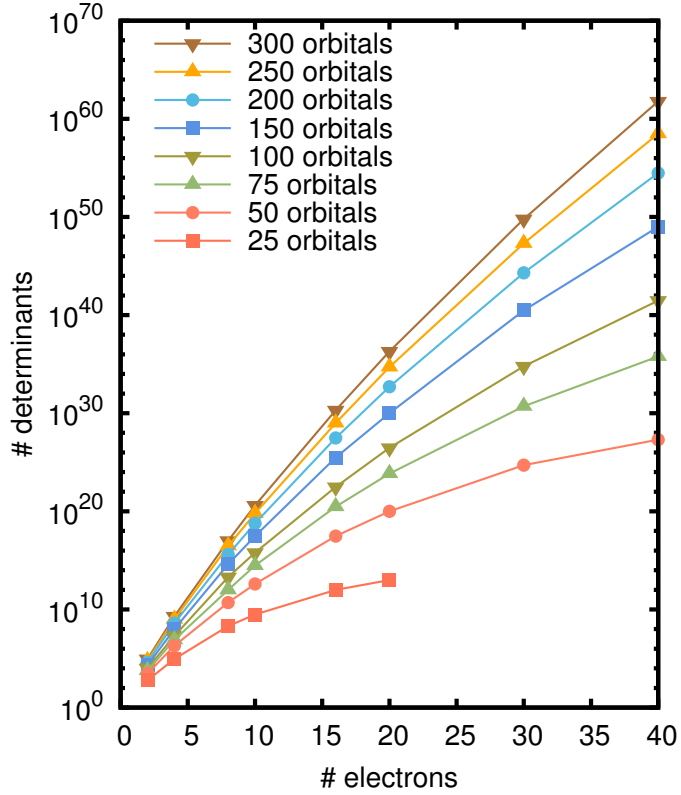


The wavefunction is written with **determinants**.

$$\text{cost} \propto \binom{\#\text{orb}}{\#\uparrow}\binom{\#\text{orb}}{\#\downarrow}$$

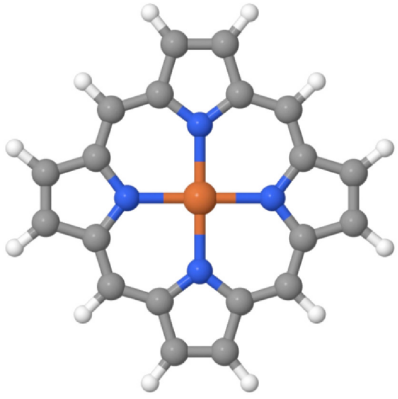
In multireference methods, one chooses a subset of orbitals and a subset of electrons, defining an **active space**, hopefully treated exactly:

$$|\Psi\rangle = \sum c_i |D_i\rangle$$



→ **For any given method, the size of the tractable active space is crucial.**

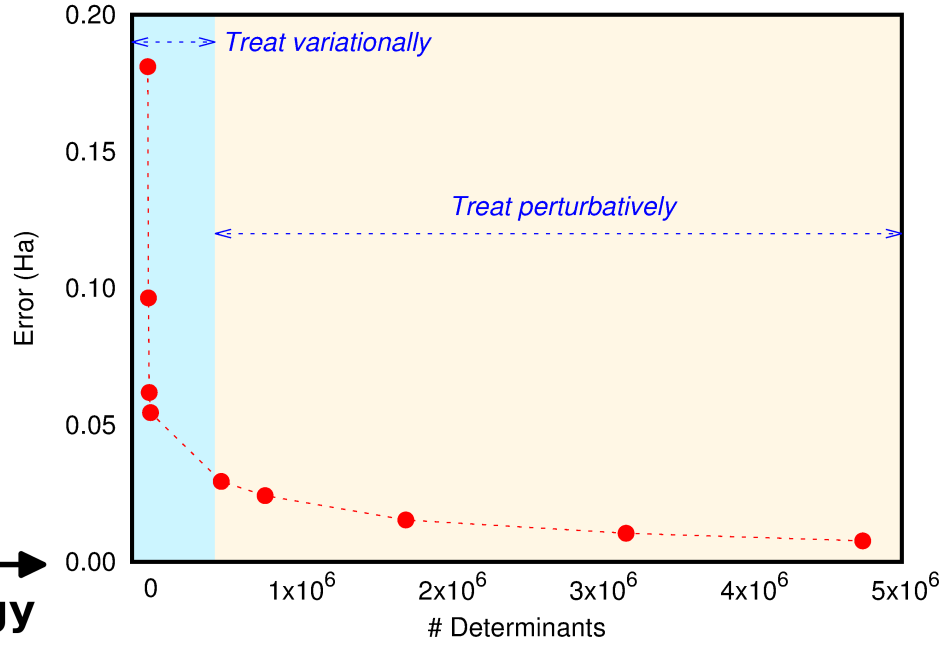
For more challenging systems, it is hard to perform exact calculations for interesting active spaces: **approximate methods are needed**.



Fe(Porphyrin)

(32e,29o)

$> 10^{15}$ determinants



Selected CI + Perturbation : Two stages

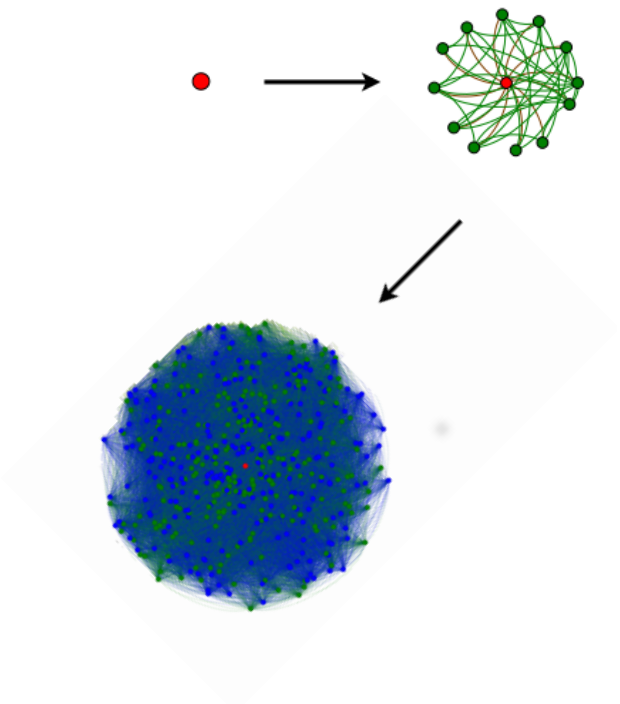
- Variational stage: calculate E_0 in a space of important det.

  → **Q1) How to quickly select "important" det.?**

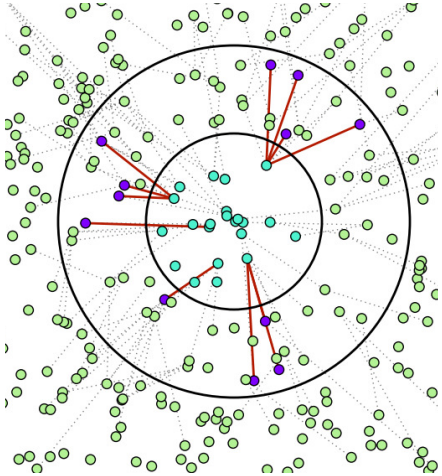
- Perturbational stage: calculate E_2

  → **Q2) How to avoid the memory bottleneck?**

→ **Iteratively find important determinants by connections to a current space.**



At a given iteration the variational space is augmented by a subset of the connected determinants.



This involves a parameter to add **a very small subset** of the connected determinant.

SHCI uses a simple criterion that allows to **easily implement a fast algorithm**.

Consider the first-order correction to the wavefunction:

$$|1\rangle = \sum_{D_a \in \mathcal{C}} \frac{\sum_{D_i \in \mathcal{V}} H_{ai} c_i}{E_0 - E_a} |D_a\rangle$$

A good criteria to include a determinant into $\mathcal{V}$ is based on:

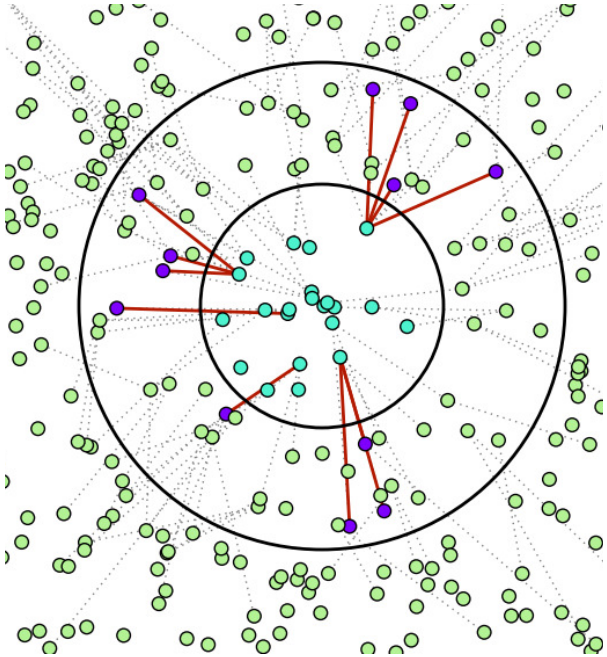
$$f(|D_a\rangle) = \frac{\sum_{D_i \in \mathcal{V}} H_{ai} c_i}{E_0 - E_a}$$

We observe that:

- the denominator $E_0 - E_a$ is fairly constant
- the numerator is dominated by $\max_{D_i \in \mathcal{V}} |H_{ai} c_i|$

The criteria can be safely approximated as:

$$f(|D_a\rangle) = \max_{D_i \in \mathcal{V}} |H_{ai} c_i|$$



The two criteria will pick the same determinants

$$\left\{ |D_a\rangle \;\middle|\; \max_{D_i \in \mathcal{V}} |H_{ai} c_i| > \epsilon \right\}$$

$$\downarrow$$

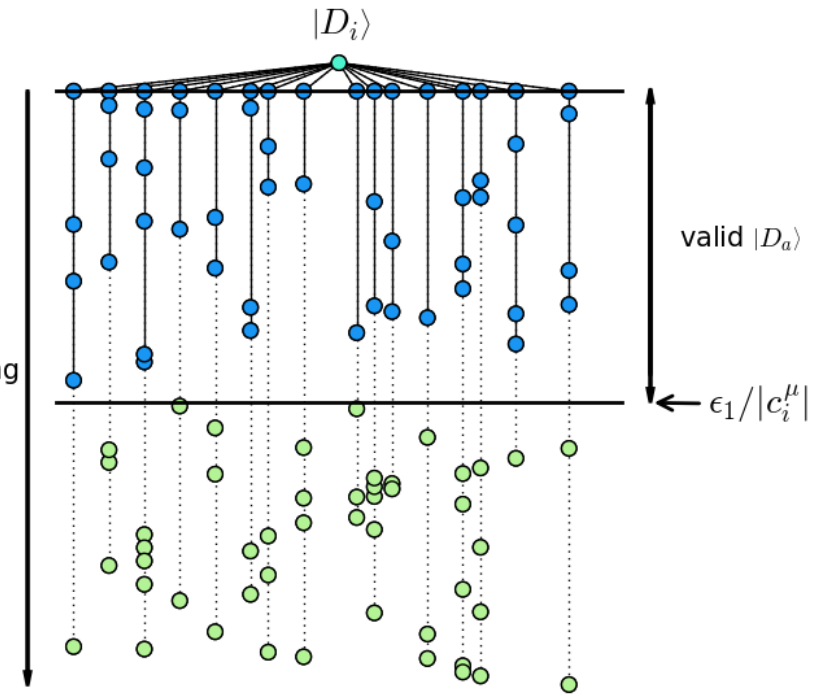
$$\left\{ |D_a\rangle \;\middle|\; \exists\, D_i \in \mathcal{V} \;/\; |H_{ai}| > \epsilon/|c_i| \right\}$$

$$\downarrow$$

$$\bigcup_{D_i \in \mathcal{V}} \left\{ |\hat{E}^{rs}_{pq} D_i\rangle \;\middle|\; |H^{rs}_{pq}| > \epsilon/|c_i| \right\}$$

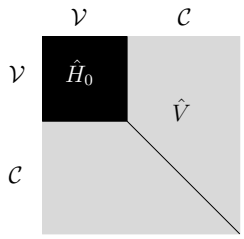
$H_{ai} = \langle D_a|\hat{H}|D_i\rangle$ depends only on the orbitals that change between D_a and D_i

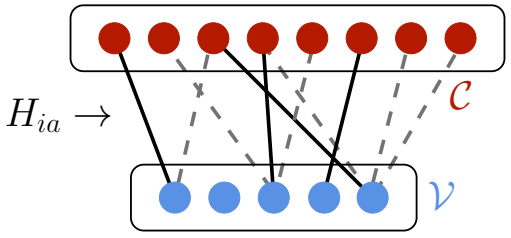
$$H_{ia} = \left\langle \; \middle| \hat{H} \middle| \; \right\rangle = H^{rs}_{pq} = \left\langle \; \middle| \hat{H} \middle| \; \right\rangle = H_{jb}$$



We loop through determinants in $\mathcal{V}$ and generate for each all the excited determinants for which H^{rs}_{pq} is above a i-dependent threshold.

$$|1\rangle = \frac{1}{\hat{H}_0 - E_0}\hat{V}\,|0\rangle$$





too memory intensive!

$e^2 v^2 N_{\mathcal{V}}$

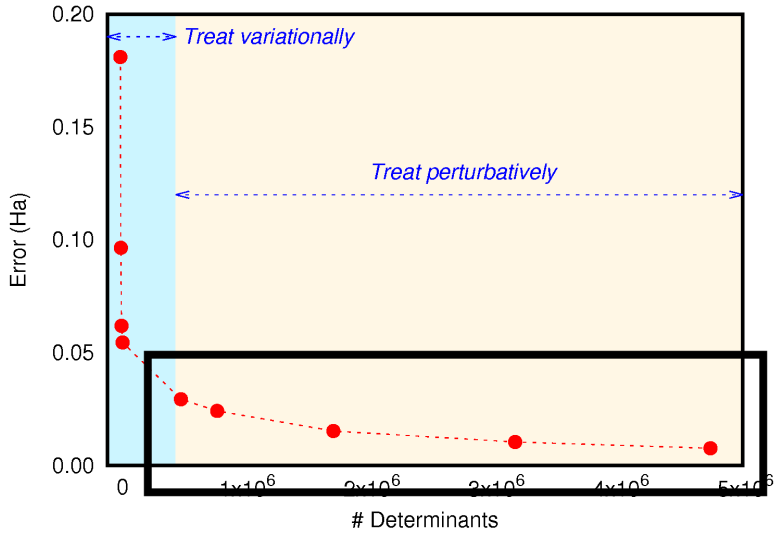
$\approx 20^2 100^2 10^7$

$\approx 10^{12}$

Truncated summation

$$E_2[\text{trunc.}] = \sum_{D_a \in \mathcal{C}(\epsilon)} \frac{1}{E_a - E_0}\left(\sum_{D_i \in \mathcal{V}}^{(\epsilon)} H_{ai} c_i\right)^2$$

The size of the sum is very sensitive to the truncation threshold



Stochastic expression

For the same reason: this lends itself to a stochastic treatment!

$$\langle E_2 \rangle = \langle 0|\hat{V}\frac{1}{\hat{H}_0 - E_0}\hat{V}|0\rangle$$

Semistochastic implementation

$$E_2[\text{trunc.}] + \left(\langle E_2 \rangle - \langle E_2[\text{trunc.}] \rangle\right)$$

$$E_2 = \sum_{D_a \in \mathcal{C}} \frac{1}{E_a - E_0} \left(\sum_{D_i \in \mathcal{V}} H_{ai} c_i \right)^2$$

Semistochastic implementation

$$E_2[\text{trunc.}] + \left(\langle E_2 \rangle - \langle E_2[\text{trunc.}] \rangle \right)$$

❶ ❷ ❸ ❹

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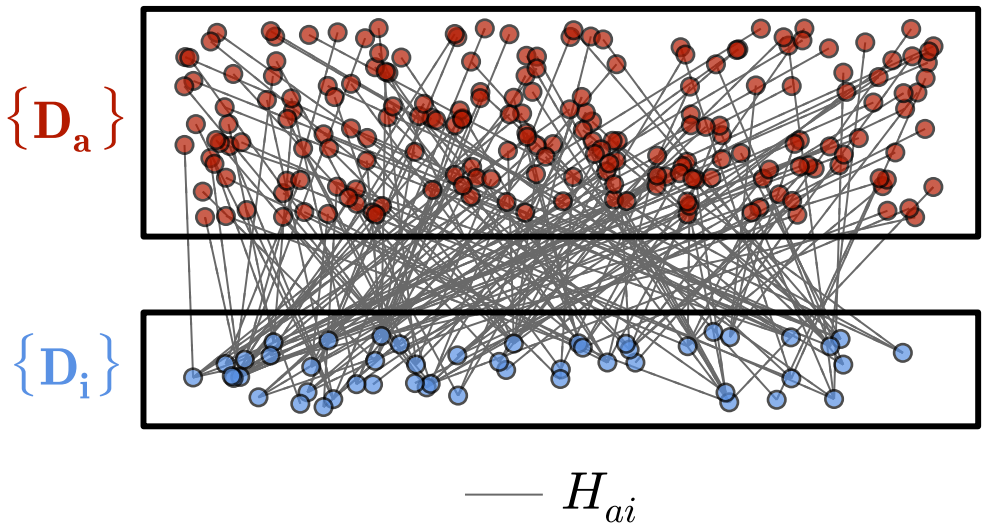
❶ : the naive PT correction is too expensive to calculate with **a purely brute force approach**.



$$E_2 = \sum_{D_a \in \mathcal{C}} \frac{1}{E_a - E_0} \left(\sum_{D_i \in \mathcal{V}} H_{ai} c_i \right)^2$$

Semistochastic implementation

$$E_2[\text{trunc.}] + \left(\langle E_2 \rangle - \langle E_2[\text{trunc.}] \rangle \right)$$

❶ ❷ ❸ ❹

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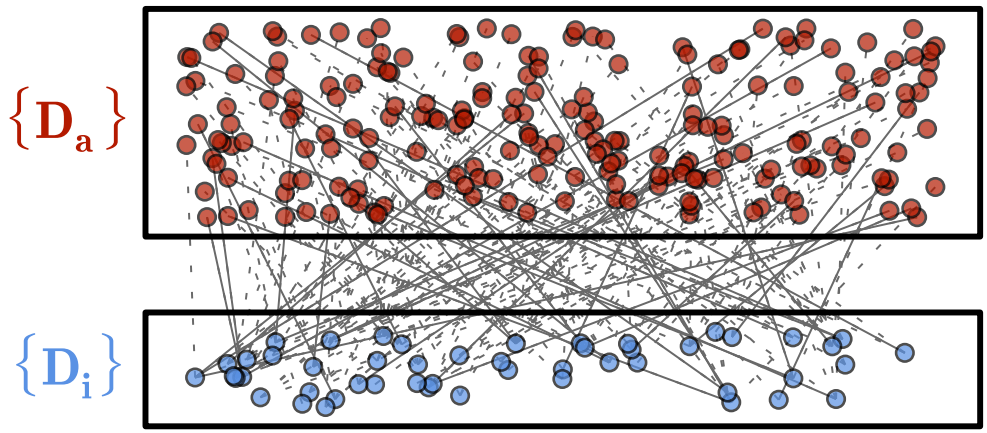
❷ : the summation is truncated based on $|H_{ia}|$.

This is still very expensive, but one can cut the summation depending on computer ressources.

The error is quite uncontrolled.



$$E_2 = \sum_{D_a \in \mathcal{C}} \frac{1}{E_a - E_0} \left(\sum_{D_i \in \mathcal{V}} H_{ai} c_i \right)^2$$

Semistochastic implementation

$$E_2[\text{trunc.}] + \left(\langle E_2 \rangle - \langle E_2[\text{trunc.}] \rangle \right)$$

1 2 3 4

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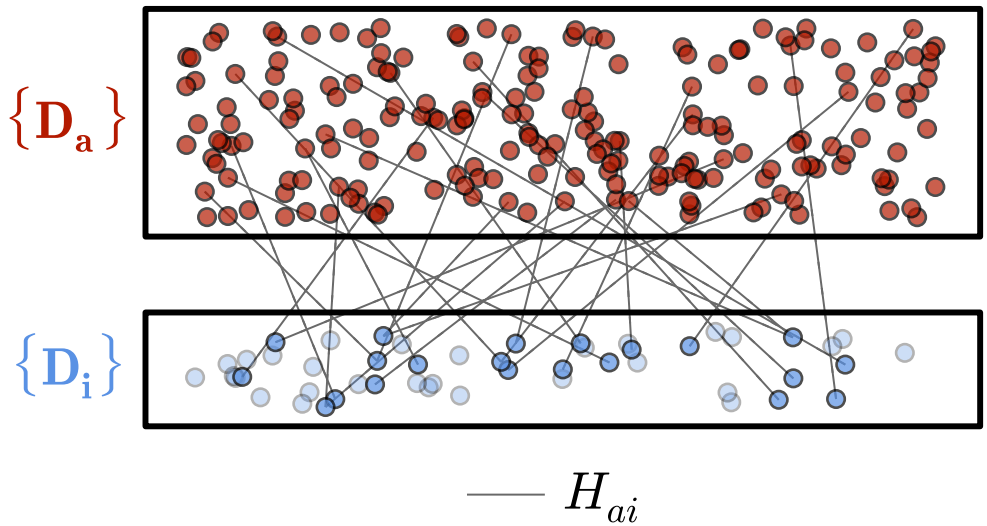
3 : the PT is evaluated **stochastically**.

The situation is good for this approach.



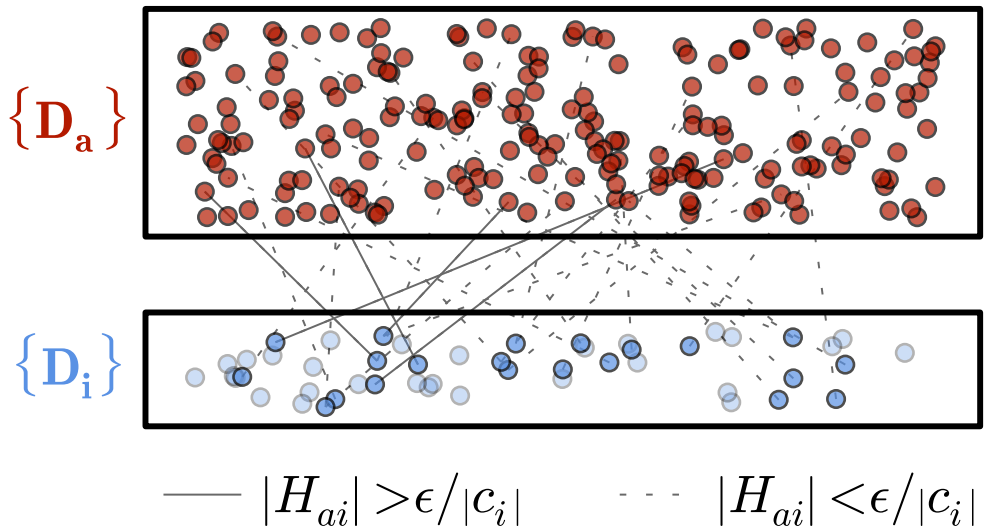
$$E_2 = \sum_{D_a \in \mathcal{C}} \frac{1}{E_a - E_0} \left(\sum_{D_i \in \mathcal{V}} H_{ai} c_i \right)^2$$

Semistochastic implementation

$$E_2[\text{trunc.}] + \left(\langle E_2 \rangle - \langle E_2[\text{trunc.}] \rangle \right)$$

1 2 3 4

4 : the PT is evaluated stochastically
AND truncated based on $|H_{ia}|$.

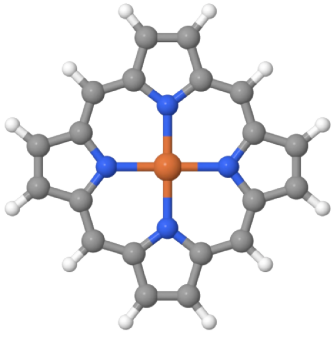


A

Self-consistent field feature

Going from near-exact CASCI with large active spaces to near-exact **CASSCF with large active spaces**.

[Smith,**BM**,Holmes,Sharma JCTC (2017)]

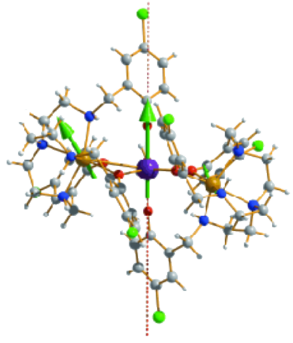


B

Spin-orbit coupling

Variational treatment of **relativistic effects** with large active spaces.

[**BM**,Sharma JCTC (2017)]

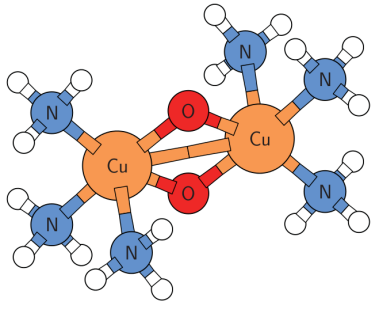


C

Dynamical correlation

Tackle static and dynamical correlation with an **internally contracted MRPT**.

[**BM**,Sharma (in prep.)]



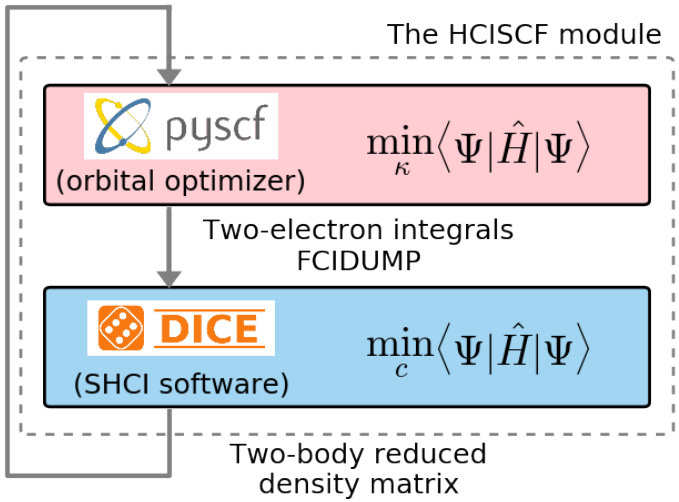
Orbital Optimization

$E_{\text{SHCI}} = E_0 + E_2$ is not variational wrt. to its parameters:

$$\partial E \neq \langle 0|\partial \hat{H}_0|0\rangle$$

We use the **Lagrangian formalism** to get the analytical gradient:

$$\partial E = \langle 0|\partial \hat{H}_0|0\rangle + (\text{lagrangian terms})$$

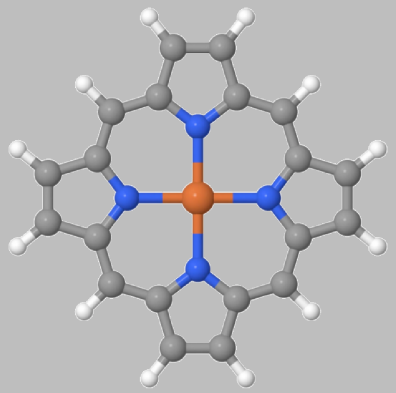


Leads to faster convergence of an individual SHCI run.

Note: the equations to derive the gradient wrt the orbital parametrization are similar to the equations of the **gradient wrt the nuclear coordinates** (➡ **geometry optimizations**,. . .)
[Smith,**BM**,Sharma (in prep.)]

[Smith,**BM**,Holmes,Sharma JCTC (2017)]

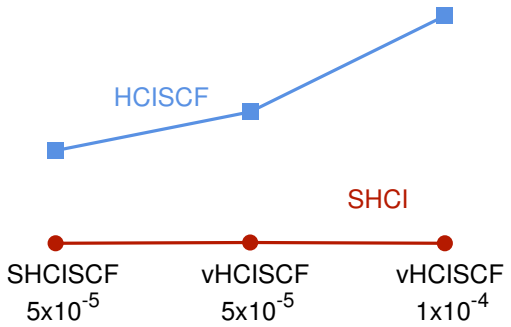
Fe(Porphyrin)



Model of the active site of the heme group

Effect of the orbitals

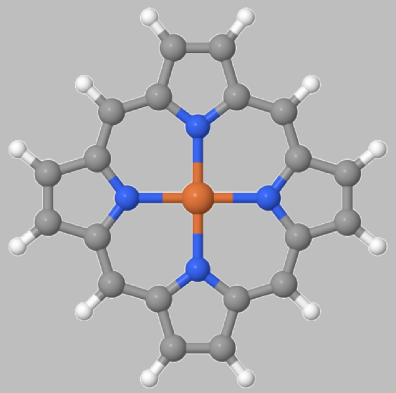
	ϵ_1	E_{SHCISCF}	E_{SHCI}
SHCISCF orbitals	5.10^{-5}	-2245.0178	-2245.0314
vHCISCF orbitals	5.10^{-5}	-2245.0121	-2245.0313
vHCISCF orbitals	1.10^{-4}	-2244.9980	-2245.0314



→ **A quick vHCISCF calculation is enough to obtain converged active space orbitals.**

[Smith,**BM**,Holmes,Sharma JCTC (2017)]

Fe(Porphyrin)



Model of the active site of the heme group

Large active spaces

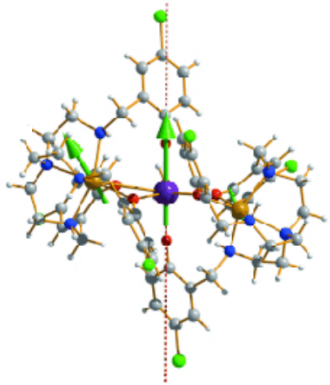
	E_{SHCI}	E_{ex}
cc-pVDZ (32e,29o)		
^5A_g	-0.0314(5)	16.7
$^3B_{1g}$	-0.0049(6)	
cc-pVTZ (32e,29o)		
^5A_g	-0.2549(5)	16.4
$^3B_{1g}$	-0.2288(6)	
cc-pVDZ (44e,44o)		
^5A_g	-0.1964(9)	**-2.0**
$^3B_{1g}$	-0.1995(6)	

→ **Need to include Fe-N bonding and anti-bonding and a second *d* shell**

[Smith,**BM**,Holmes,Sharma JCTC (2017)]

Relativistic effects

- important to capture phosphorescence, magnetism, hyperfine constant, g-tensors,. . .
- comparable to electron correlation in heavy atoms.



Challenge

$\hat{H} = \hat{H}_{\text{SR}} + \hat{H}_{\text{SOC}}$
where $\langle n_\alpha n_\beta | \hat{H}_{\text{SOC}} | n'_\alpha n'_\beta \rangle \neq 0$

State of the art methods
use a 2-step process with QDPT:

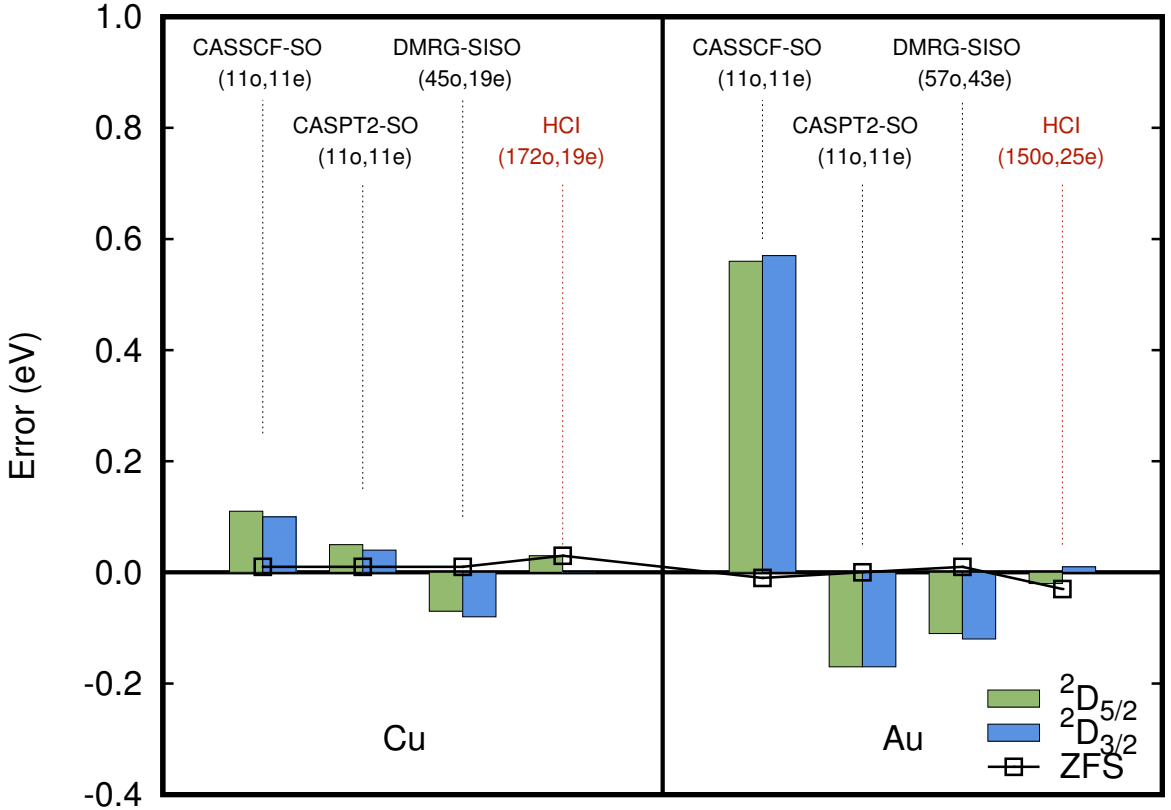
1) obtain $|1\rangle, \ldots, |N\rangle$ of $\hat{H}_{\text{SR}}$
2) diagonalize $\langle i | \hat{H}_{\text{SR}} + \hat{H}_{\text{SOC}} | j \rangle$

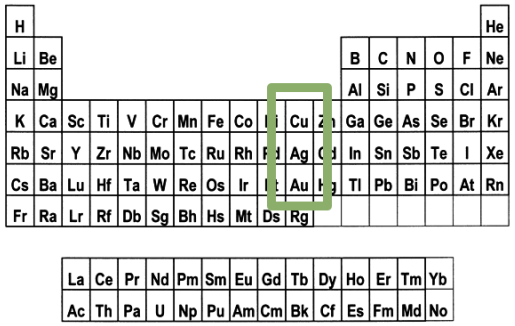
→ **In our approach, SHCI treats relativistic effects with large active spaces in a one-step procedure on an equal footing with correlation.**

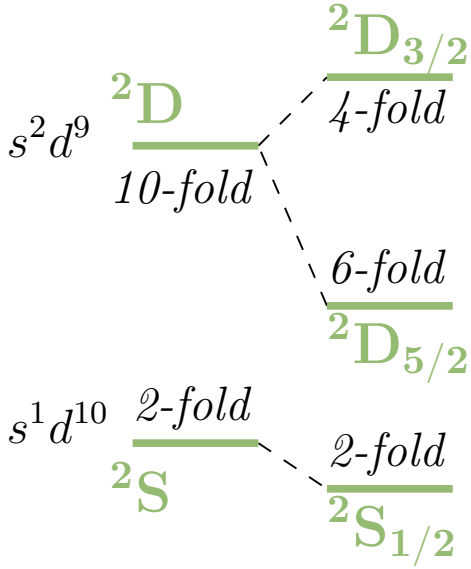
SHCI retains its ability to discard large parts of low importance in the increased-size Hilbert space.

[**BM**,Sharma JCTC (2017)]

Coinage metals





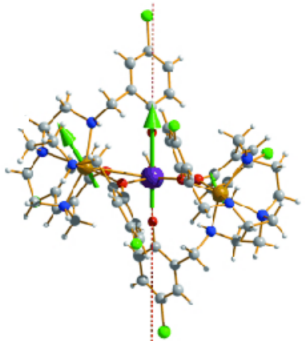


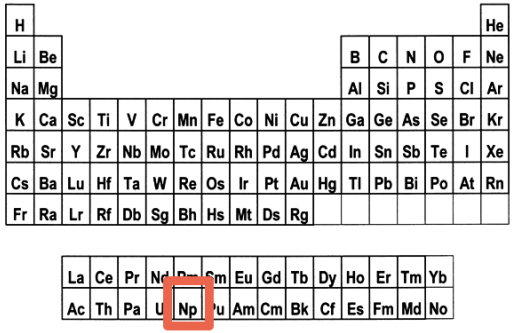
→ **Au (25e,150o): $> 10^{30}$, converged results with 10^7**

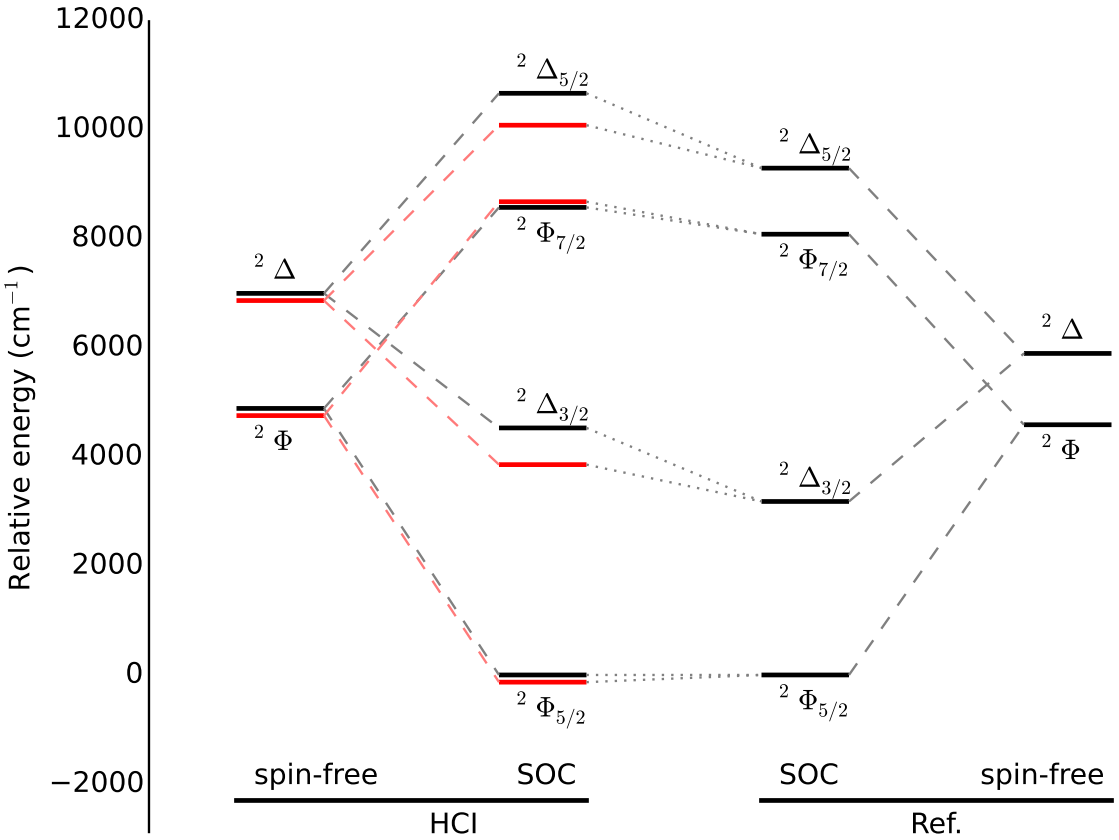
[**BM**,Sharma JCTC (2017)]

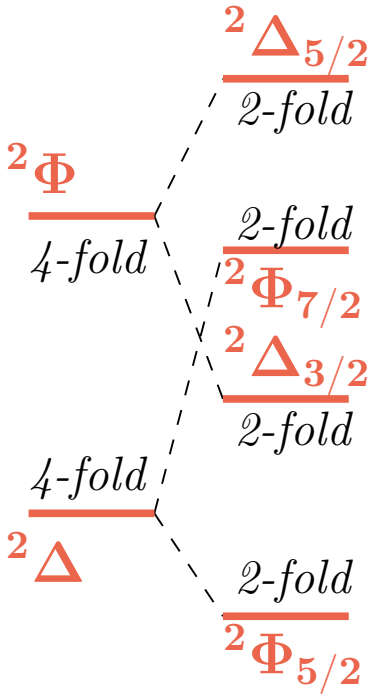
Neptunyl(VI) dioxide NpO_2^{2+}

- Insight into interesting complexes (**Single Molecular Magnets**)







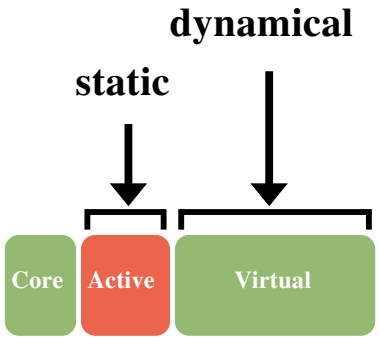


[**BM**,Sharma JCTC (2017)]

Static and dynamical correlation typically have **vastly different needs** in term of ansätz for the WFT.

- static correlation typically needs high flexibility in many-body configuration space
- dynamical correlation needs a large set of virtual orbitals (the many-body structure can be simple).

→ **This is generally challenging to reconcile.**



In an MR calculation, the "out-of-active space" dynamical correlation is untreated, and can be added *a posteriori*.

MRLCC (MR Linearized Coupled-Cluster)

- cheaper than MRCI+Q ; at least as accurate
- independence to the orbitals (versus MRCI)
- intruder state free (versus CASPT)

[Sharma,Alavi JCP 143 (2015)]

The first-order correction to the WFT is expanded on a basis $\{|b_I\rangle\}$:

$$|\mathbf{1}\rangle = \sum \boldsymbol{d}_I |b_I\rangle$$

where the coefficients $\boldsymbol{d}_I$ are found by **minimizing the Hylleraas functional**:

$$(E_0 - \hat{H}_0)|\mathbf{1}\rangle = \hat{V}|\mathbf{0}\rangle$$
$$\overset{\forall I}{\Longleftrightarrow} \langle b_I|(E_0 - \hat{H}_0)|b_J\rangle \boldsymbol{d}_J = \langle b_I|\hat{V}|\mathbf{0}\rangle$$

Internal contraction:
the basis $\{\hat{E}_I|\mathbf{0}\rangle\}$ is used:

$$A_{IJ} = \langle \mathbf{0}|\hat{E}_I^\dagger (E^{(0)} - \hat{H}_0)\hat{E}_J|\mathbf{0}\rangle$$
$$s_I = \langle \mathbf{0}|\hat{E}_I^\dagger \hat{E}_J|\mathbf{0}\rangle w_J$$

Normal-ordering A_{IJ} and s_I yields $\sim 10^3$ lines of equations for E_2 and for E_3

→ Symbolic Algebra

Tensor contractions of integrals and RDMs up to fourth-order

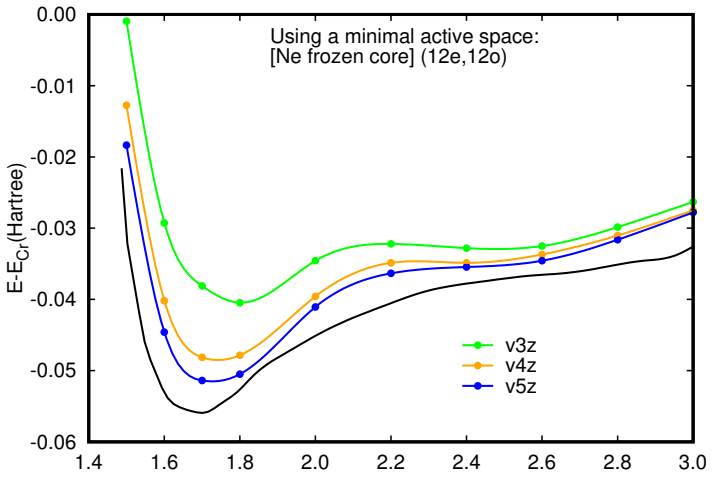
→ Tensor Contraction engine

The coefficient are found by minimization of the Hylleraas functional

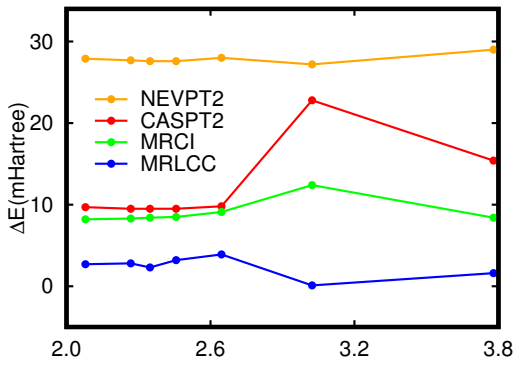
→ Minimizer for d

Properties of MRLCC

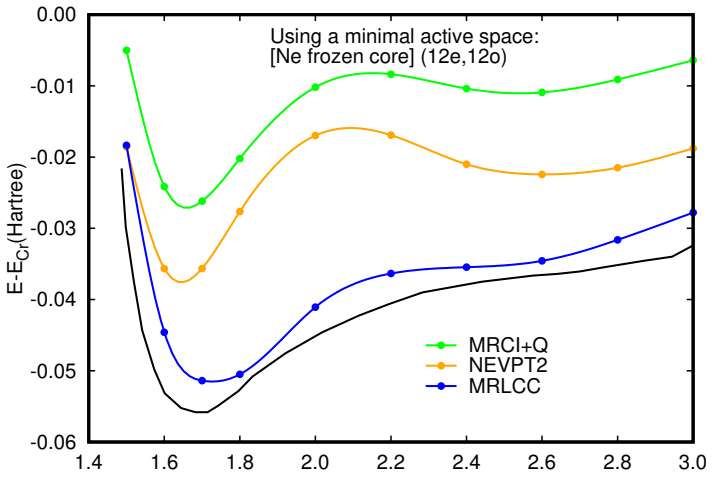
Basis dependence



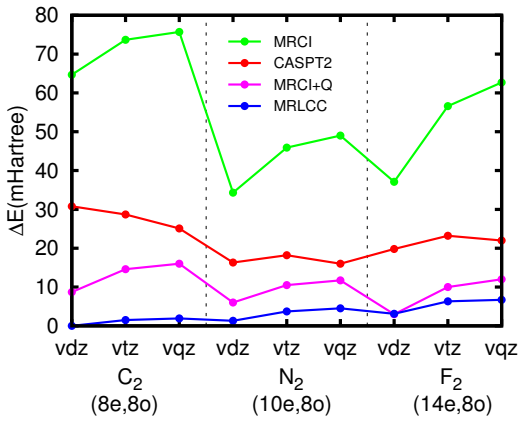
C_2 PES



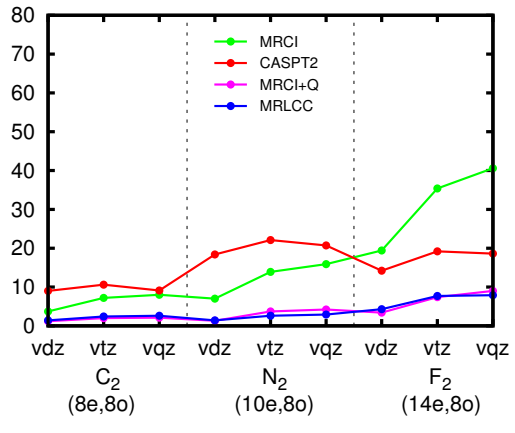
Performance on Cr_2



CASCI reference wavefunction



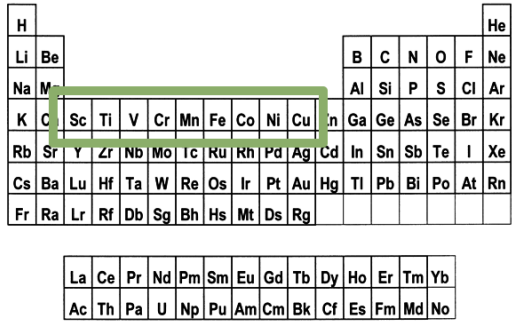
CASSCF reference wavefunction

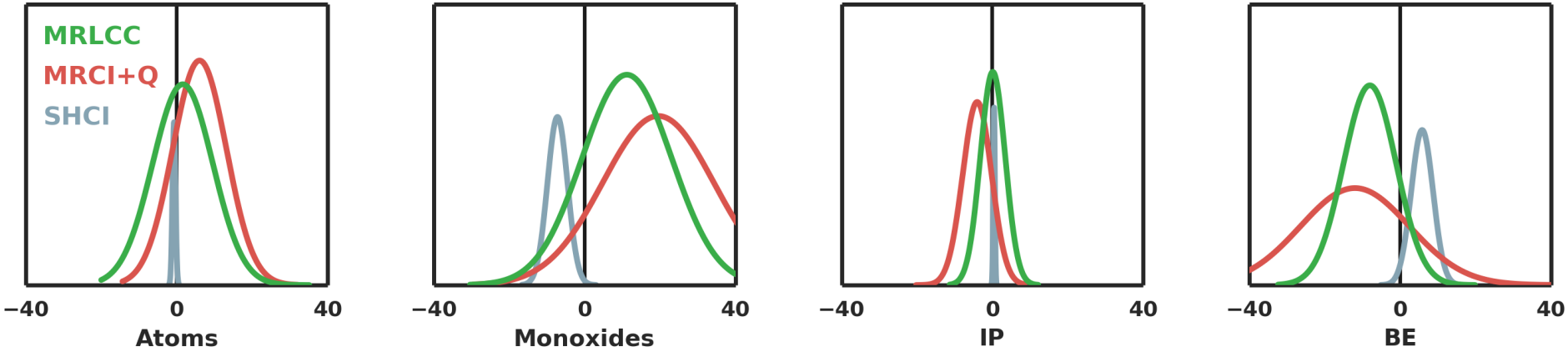


A benchmark study of transition metal oxides
is underway using various methods
(DFT, RPA, GF2, SEET, DMC, DMRG, AFQMC, . . .).

The transition metal oxides involved are
ScO, TiO, VO, CrO, MnO, FeO, CuO.

The quantities at play are the **energies** of the neutral atoms, cations and monoxides, as well as **ionization and dissociation energies**.





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

Dice is interfaced with PySCF, a widely-used *ab initio* computational chemistry program implemented in Python/C and available with `pip`

Welcome to Dice's documentation!

Dice implements the semistochastic heat bath configuration interaction (SHCI) algorithm for *ab initio* Hamiltonian of a quantum chemical system. Unlike full configuration interaction (FCI), SHCI can be used to treat active spaces containing 30-100 orbitals. SHCI is able to accomplish this by taking advantage of the fact that although the full Hilbert space may be enormous, only a small fraction of the determinants in the space have appreciable coefficients. Compared to other methods in its class SHCI is often not only orders of magnitude faster, it also does not suffer from a serious memory bottleneck that plauges such methods. The resulting algorithm as implemented in Dice allows us to treat difficult benchmark systems such as the Chromium dimer and Mn-Salen (a challenging bioinorganic cluster) at a cost that is often an order of magnitude faster than either density matrix renormalization group (DMRG) or full configuration interaction quantum Monte Carlo (FCIQMC). Thus if you are interested in performing multireference calculations with active space containing several tens to hundreds of orbitals, SHCI might be an ideal choice for you.

Contents: