

**Cheap and near exact calculations
with large active spaces.**

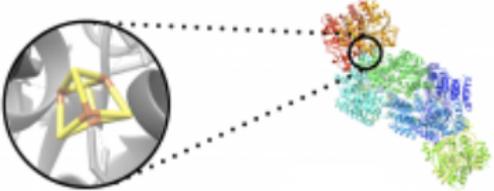
New applications for the “SHCI” algorithm

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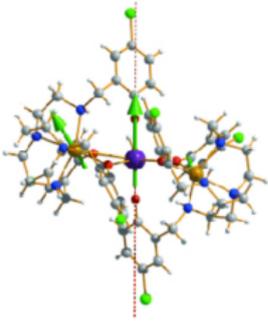
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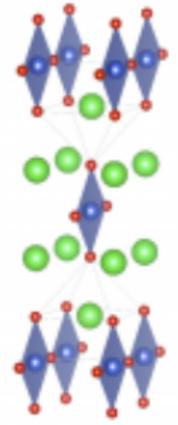
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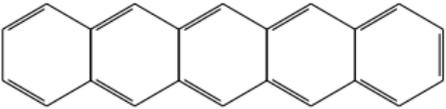
Model systems for catalysis



Lanthanide complexes



Transition metal oxides



Acenes

The systems of interest in biological processes, in energy conversion, in energy storage, ... are challenging because of **static and dynamical correlation**.

The wavefunction is written with **determinants**.

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

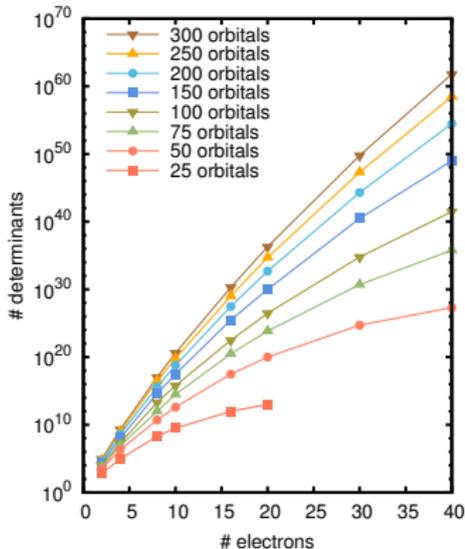
$$|\Psi\rangle = \sum_{D_n \in \text{Active}} c_n |D_n\rangle$$

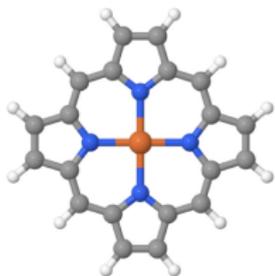


→ For any given method, the size of the tractable active space is crucial.

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

$$\text{cost} = \left(\frac{\#\text{orb}}{\#\text{elec}/2} \right)^2$$



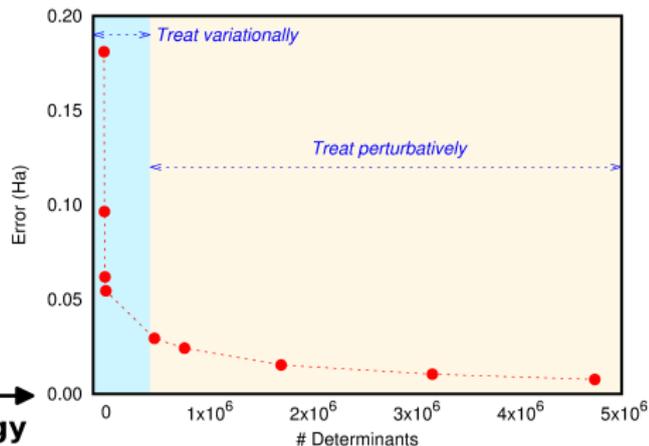


Fe(Porphyrin)

(32e,29o)

> 10^{15} determinants

CAS →
energy



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?

CIPSI (CI Perturbatively Selected Iteratively)

The original idea comes from here.

CIPSI is used a lot notably together with FN-QMC.



[Giner *et. al.* CJC (2013)]

[Scemama *et. al.* JCC (2016)]

[Garniron *et. al.* JCP (2017)]

SHCI (Semistochastic Heat-bath CI)

An alternative algorithm based on the same basic idea.

SHCI is used in an SCF context and includes relativistic effects.



[Holmes *et. al.* JCTC (2016)]

[Sharma *et. al.* JCTC (2017)]

[Mussard *et. al.* JCTC (2017)]

And many, many, many other implementations

Adaptative CI

Iterative CI

(energy-based for QMC)

SCI/MCCI

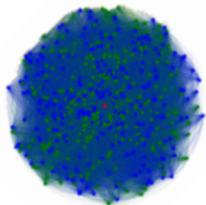
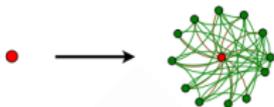
[Evangelista JCP (2014)]

[Liu JCTC (2016)]

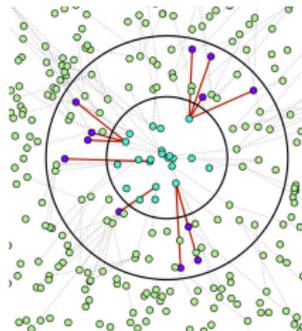
[Per JCP (2017)]

[Ohtsuka JCP (2017)]

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



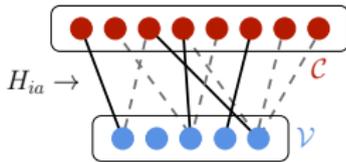
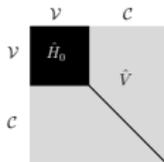
At a given iteration the variational space is augmented by a subset of the connected determinants.



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.**

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



too memory
intensive!

$$e^2 v^2 N_\nu$$

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

$$\approx 10^{12}$$

Truncated summation

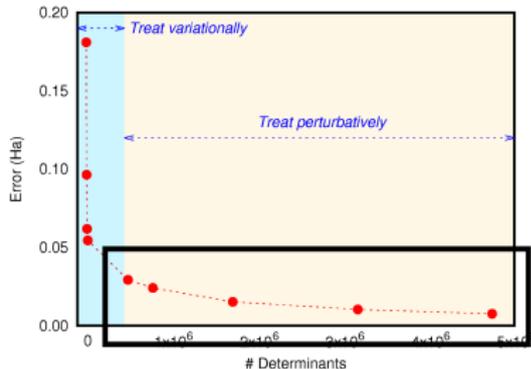
$$E_2[\text{trunc.}] = \sum_{D_a \in \mathcal{C}(\epsilon)} \frac{1}{E_a - E_0} \left(\sum_{D_i \in \mathcal{V}}^{(\epsilon)} H_{ai} C_i \right)^2$$

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!

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

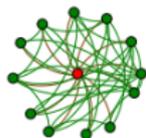


Semistochastic implementation

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

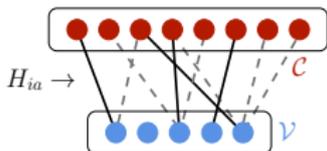
$$\text{SHCI} = E_0 + E_2$$

Variational



+

Semistoch. PT



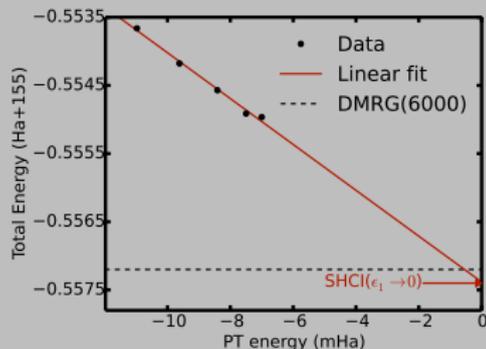
→ One-parameter algorithm
to obtain the CASCI energy
with a large active space.

This parameter simply depends on the resources available for a calculation.

We have a built-in method to automatically **extrapolate** to the exact result.

Butadiene

(22e,82o)



ϵ_1	N_{var}	vHCI	SHCI
3.10^{-5}	1.10^7	-0.5411	-0.5534(1)
2.10^{-5}	2.10^7	-0.5441	-0.5540(1)
1.10^{-5}	6.10^7	-0.5481	-0.5550(1)
SHCI($\epsilon_1 \rightarrow 0$)			-0.5574(8)
DMRG(M=6000)			-0.5572

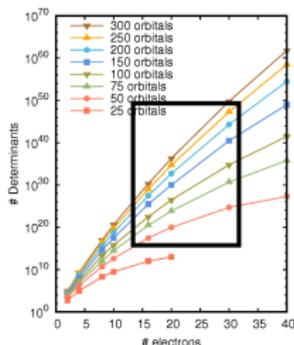
Are those algorithms “active space choosers”?

No! This is to get the near-exact CASCI energy for large active spaces. One still needs to provide an active space.

The input is of less crucial importance, since the AS can be large.

How big an active space can we reach?

First row dimers	(14e, 108o)	Butadiene	(22e, 82o)
Halogens	(17e, 121o)	oxo-Mn(Salen)	(28e, 22o)
Coinage metals	(19e, 172o)	Neptunium dioxide	(17e, 143o)
	(25e, 150o)		



How fast are those algorithms?

The time to convergence is

- from a few minutes on single core [Cr₂ (24e, 42o)],
- to 20 min on a node [Cr₂ (12e, 190o)],
- to 2 days on 8 nodes [Cr₂ (28e, 288o)].

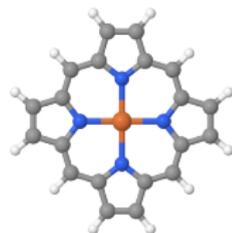
Most parts of the algorithms easily parallelizes.

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)]

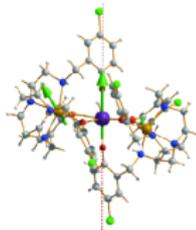


B

Spin-orbit coupling

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

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

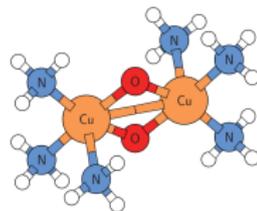


C

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:

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

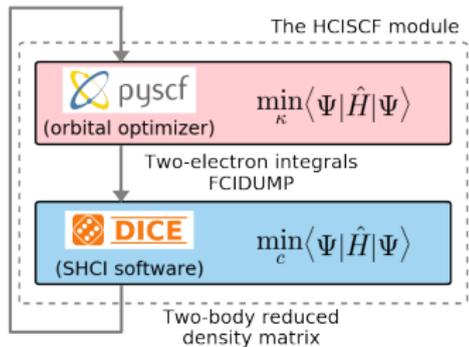
We use the **Lagrangian formalism** to get the analytical gradient:

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

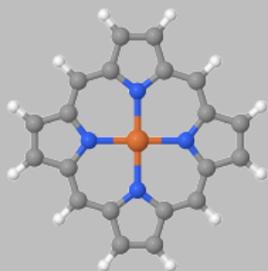
Note: the equations to derive the gradient wrt the orbital parametrization are similar to the equations of the **gradient wrt the nuclear coordinates**

(➔ **geometry optimizations**, ...)

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



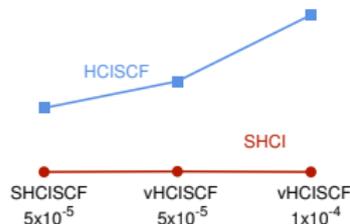
Leads to **faster convergence** of an individual SHCI run.

Fe(Porphyrin)

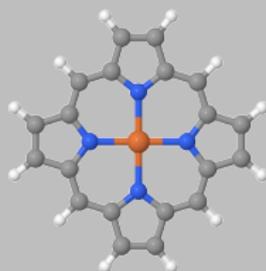
Model of the active site
of the heme group

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.

Fe(Porphyrin)

Model of the active site
of the heme group

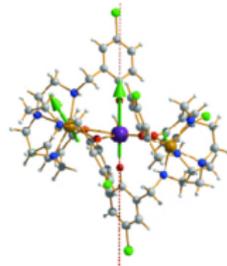
Large active spaces

	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

Relativistic effects

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



Challenge

$$\hat{H} = \hat{H}_{\text{SR}} + \hat{H}_{\text{SOC}}$$

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

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

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

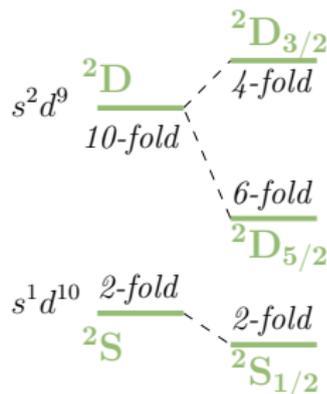
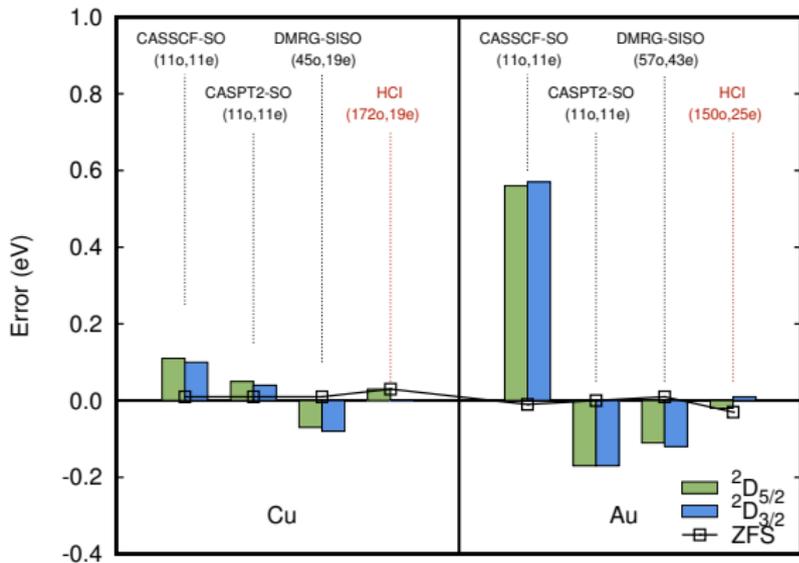
→ In our approach, SHCI treats relativistic effects with large active spaces in a one-step procedure on an equal footing with correlation.

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

Coinage metals

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg								

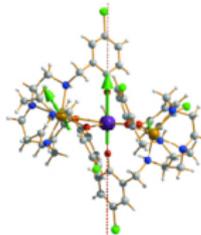
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No



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

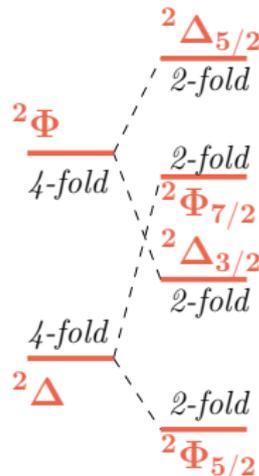
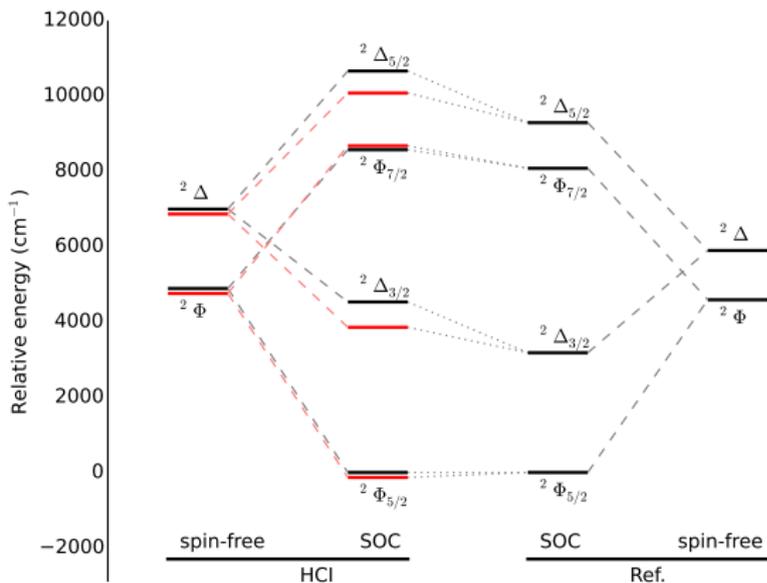
Neptunyl(VI) dioxide NpO_2^{2+}

- Insight into interesting complexes (Single Molecular Magnets)



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

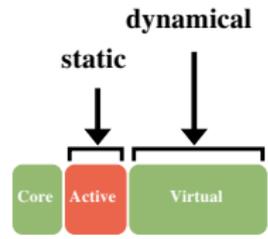
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No



Static and dynamical correlation typically have **vastly different needs** in term of ansatz 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)

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

$$|1\rangle = \sum d_I |b_I\rangle$$

where the coefficients d_I are found by **minimizing the Hylleraas functional**:

$$(E_0 - \hat{H}_0) |1\rangle = \hat{V} |0\rangle$$

$$\overset{\forall I}{\iff} \langle b_I | (E_0 - \hat{H}_0) | b_J \rangle d_J = \langle b_I | \hat{V} | 0 \rangle$$

Internal contraction:

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

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

$$s_I = \langle 0 | \hat{E}_I^\dagger \hat{E}_J | 0 \rangle w_J$$

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

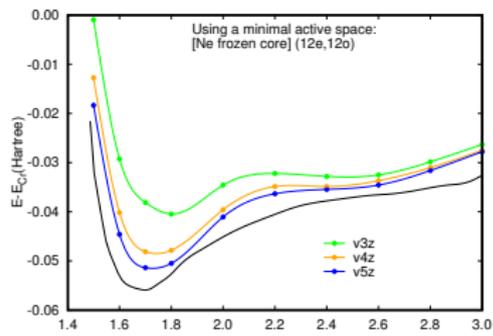
→ Tensor Contraction engine

The coefficient are found by minimization of the Hylleraas functional

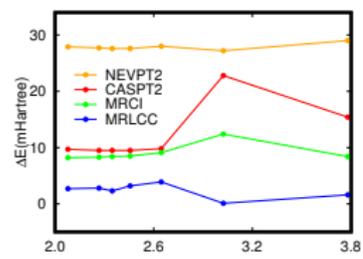
→ Minimizer for d

Properties of MRLCC

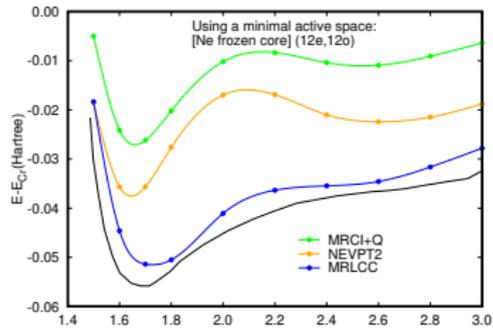
Basis dependence



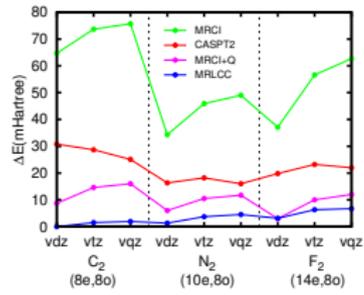
C₂ PES



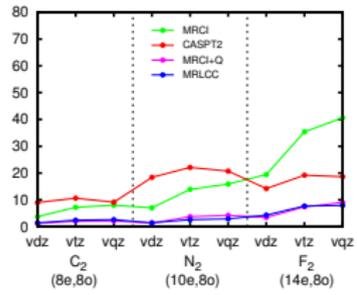
Performance on Cr₂



CASCI reference wavefunction



CASSCF reference wavefunction



A benchmark study of transition metal oxides

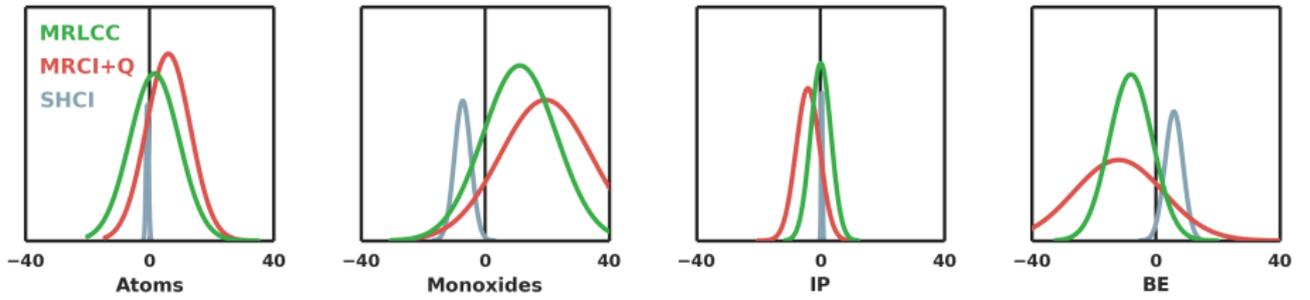
is undergoing using various methods (DFT, RPA, GF2, SEET, DMC, DMRG, AFQMC, ...).

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

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

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

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No



Sandeep Sharma's group

[[website](#)]



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Matt Mulligan
Xubo Wang

Dynamical correlation

Cumulant approximations; Further optimization of tensor contraction; Calculations of Copper oxides; **Use of ML techniques that would forego the need of RDMs altogether.**

Embedding techniques

Use techniques like MC-pDFT to tackle large systems of interest.

Spin-orbit coupling

Four-component DCB Hamiltonian exactly; Quantitative calculations for realistic systems; **Ab-initio parameters for model spin-Hamiltonian (analytical response theory).**

VMC

Use of ML minimizer to optimize large numbers of parameters of a very flexible wavefunction; Green Function VMC.

<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 this class SHCI is often not only orders of magnitude faster, it also does not suffer from a serious memory bottleneck that plagues 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:

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 - [License and how to cite](#)



Consider the first-order correction to the wavefunction:

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

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

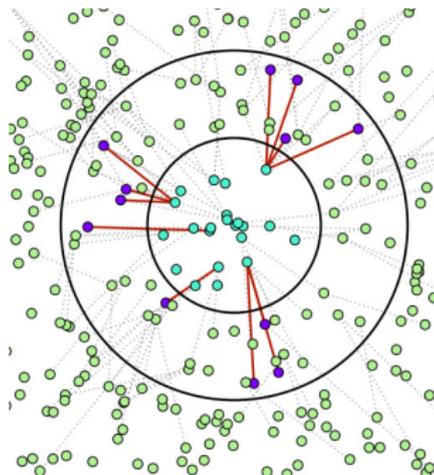
$$f^\mu(|D_a\rangle) = \frac{\sum_{D_i \in \mathcal{V}^\mu} H_{ai} c_i^\mu}{E_0 - E_a}$$

We observe that:

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

The criteria can be safely approximated as:

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



The two criteria will pick the same determinants

