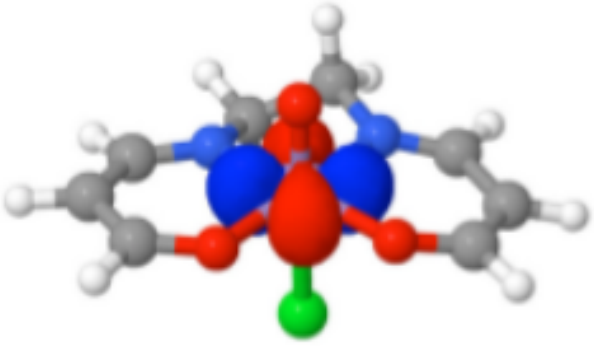
Multi-Reference Perturbation Theory using extended active space wavefunctions.

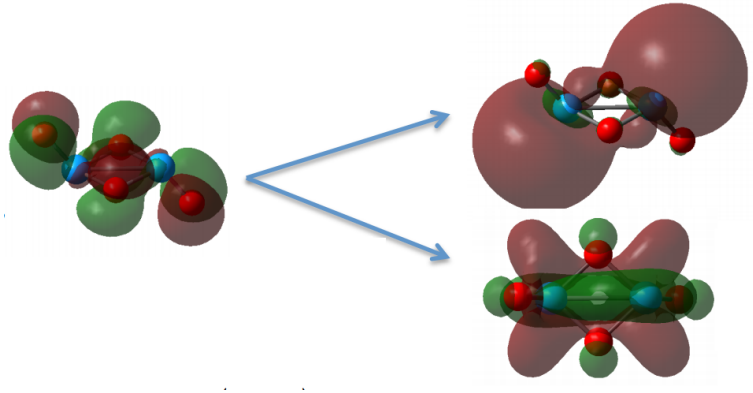
Bastien Mussard
bastien.mussard@colorado.edu
https://mussard.github.io/

Sandeep Sharma
sandeep.sharma@colorado.edu
http://www.colorado.edu/lab/sharmagroup/

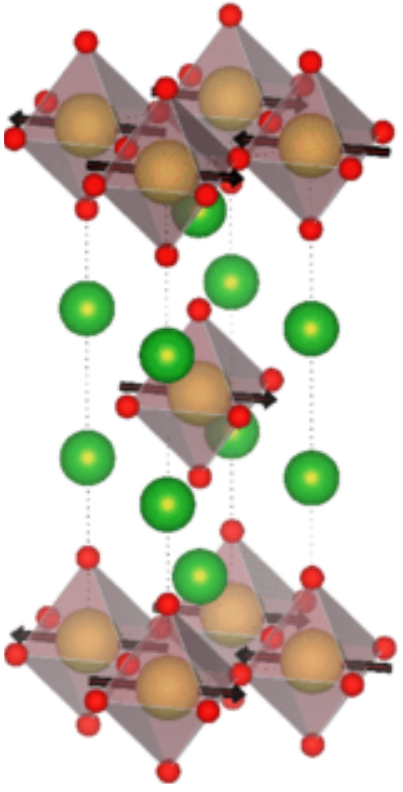
University of Colorado at Boulder



oxo-Mn Salen cluster



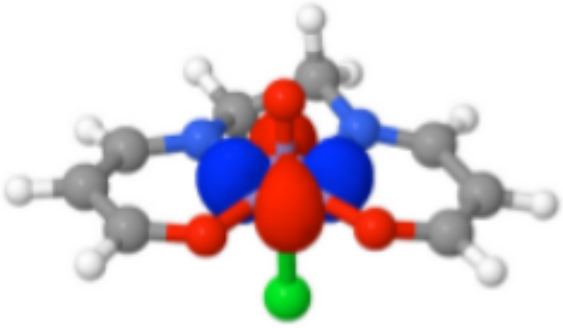
TiO_2 structure



Transition metal oxydes

The systems of interest in **biological processes**, in **energy conversion** and **energy storage** are challenging for different reasons.

These systems exhibit both large **static correlation** and **dynamical correlation** effects : they require a **multireference treatment**.



In the single-reference world :
one has a (few ?) golden standard method (**CCSD(T)**)

In the multi-reference world :
MRCI (**MRCI+Q**), MRCC (MRCCSD), MRPT (CASPT, NEVPT)

Multireference Linearized Coupled-Cluster [Sharma,Alavi JCP **143** (2015)]

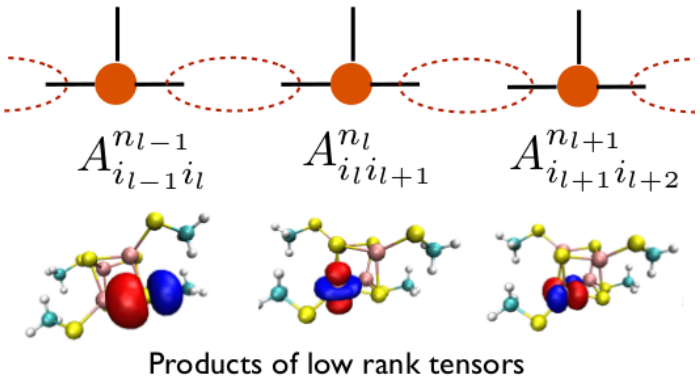
- formulated as a PT, reduces to linearized-CC for single-reference
- **cheaper than MRCI+Q**, and **at least as accurate**
- relative independence to the orbitals (versus MRCI)
- intruder state free (versus CASPT)

The bigger the **active space**, the more accurate the zero-th order wavefunction.
The cost of the subsequent PT calculation is tied to the size of the **active space**.

Density Matrix Renormalization Group (DMRG)

- the wavefunction is **factorized into products of low rank tensors** by means of singular value decomposition.
- it allows the efficient treatment of a system using a **large active space**.

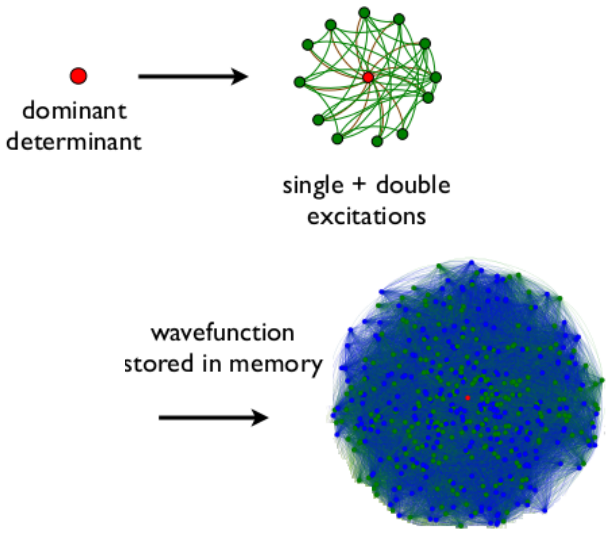
[Sharma,Chan JCP **136** (2012)]



Heat-Bath Configuration Interaction (HCI)

- a **selected CI** technique that allows to approach the FCI limit by cheaply finding the **optimal active space** to expand the wavefuntion unto.

[Holmes,Tubman,Umrigar JCTC **12** (2016)]
[Sharma *et al.* JCTC **13** (2017)]



The **connection with MRPT** is done through **reduced density matrices** (in principle : up to 4th order).

[Sharma,Knizia,Guo,Alavi JCTC **13** (2017)]

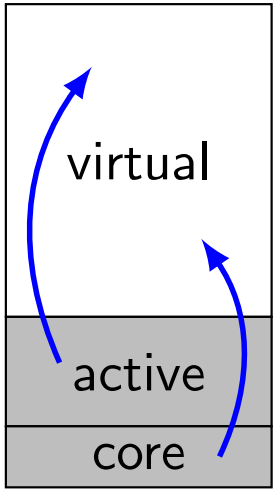
Rayleigh-Schrödinger :

$$\left| \begin{array}{l} \hat{H} = \hat{H}_0 + \hat{V} \\ \text{with : } \hat{H}_0 \left|\Psi^{(0)}\right\rangle = E^{(0)} \left|\Psi^{(0)}\right\rangle \end{array} \right. \qquad \left| \begin{array}{ll} E^{(2)} & = \left\langle \Psi^{(0)} \right| \hat{V} \left| \boldsymbol{\Psi^{(1)}} \right\rangle \\ E^{(3)} & = \left\langle \boldsymbol{\Psi^{(1)}} \right| \hat{V} - E^{(1)} \left| \boldsymbol{\Psi^{(1)}} \right\rangle \end{array} \right.$$

There is multiple possible choices for $\hat{H}_0$ under that constraint :

- **CASPT** uses the Fock operator $\hat{H}_{\text{Fock}} = \hat{P}\hat{F}\hat{P}$
  - prone to the infamous intruder state problem
  - **widely used**
- **NEVPT** uses the Dyall Hamiltonian $\hat{H}_{\text{Dyall}} = f_i^j \hat{E}_i^j + f_p^q \hat{E}_p^q + f_a^b \hat{E}_a^b + W_{pq}^{rs} \hat{E}_{pq}^{rs}$
  - **intruder state free**
  - fairly dependent of the reference calculation
- **MRLCC** uses the Fink Hamiltonian $\hat{H}_{\text{Fink}} = \left(t_u^v \hat{E}_u^v + W_{uv}^{wx} \hat{E}_{uv}^{wx}\right)\Big|_{\Delta=0}$
  [Sharma,Alavi JCP **143** (2015)] [Fink CPL **428** (2006)]
  - **intruder state free**
  - **fairly independent of the reference calculation**

The first-order correction to the wavefunction $|\Psi^{(1)}\rangle$ lives in the **perturber space**, composed of all single and double excitations on all the determinants of the zero-th order wavefunction.



It is expressed in a basis of "**perturber wavefunctions**" $b = \{|b_I\rangle\}$:

$$|\Psi^{(1)}\rangle = \sum \mathbf{d_I} |b_I\rangle$$

The coefficients $\mathbf{d_I}$ are found by minimizing the Hylleraas functional :

$$\langle b_J|(E^{(0)} - \hat{H}_0)|b_I\rangle \mathbf{d_I} = \langle b_J|\hat{V}|\Psi^{(0)}\rangle$$

Uncontracted scheme

The full basis $b = \{\hat{E}_I |D_n\rangle\}$ of all excitations to all the determinants composing $|\Psi^{(0)}\rangle$ is used.

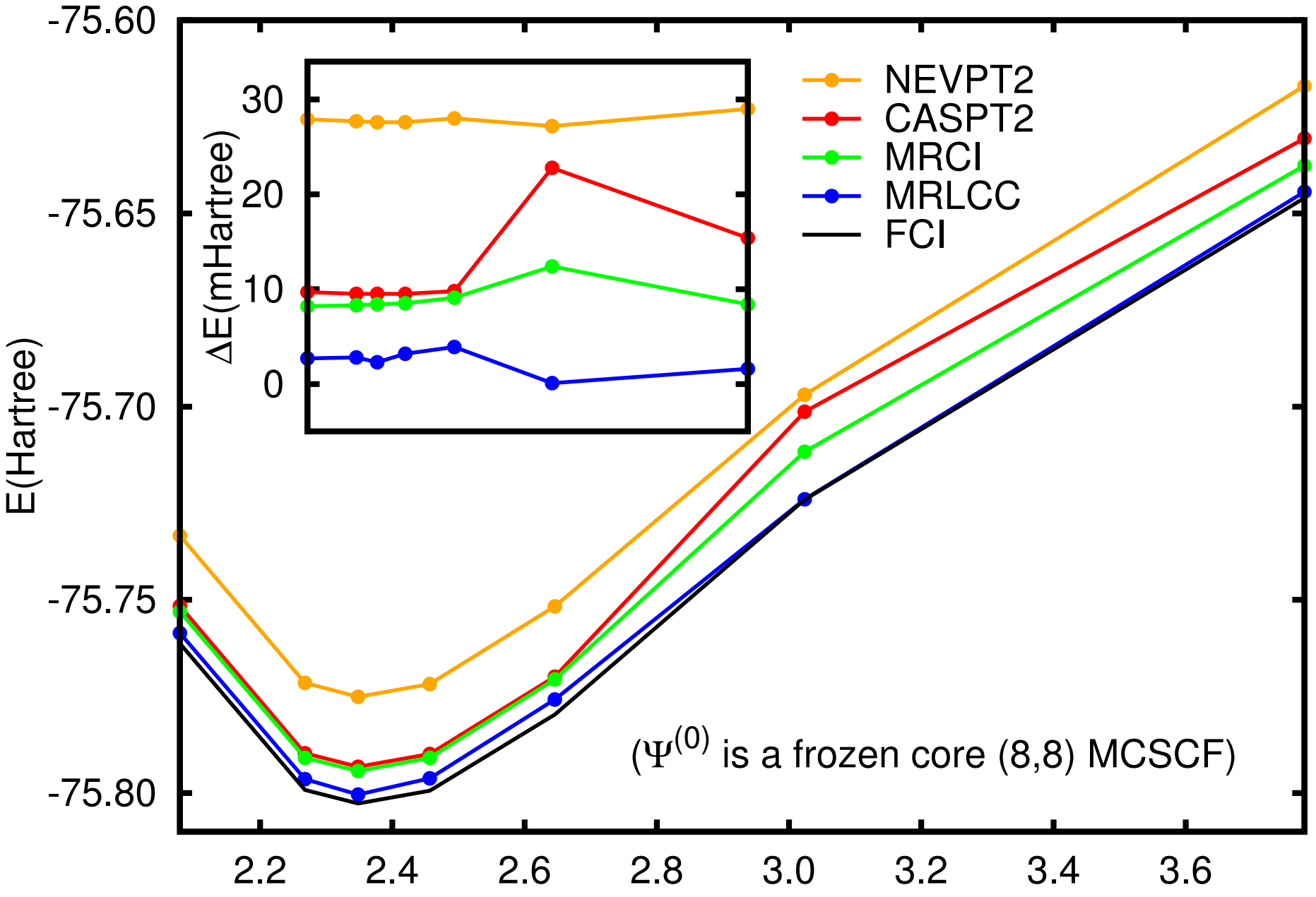
$$|\Psi^{(1)}\rangle = \sum_{I,n} \mathbf{d_{In}} \left(\hat{\mathbf{E}}_\mathbf{I} |D_n\rangle \right)$$

Internally contracted scheme

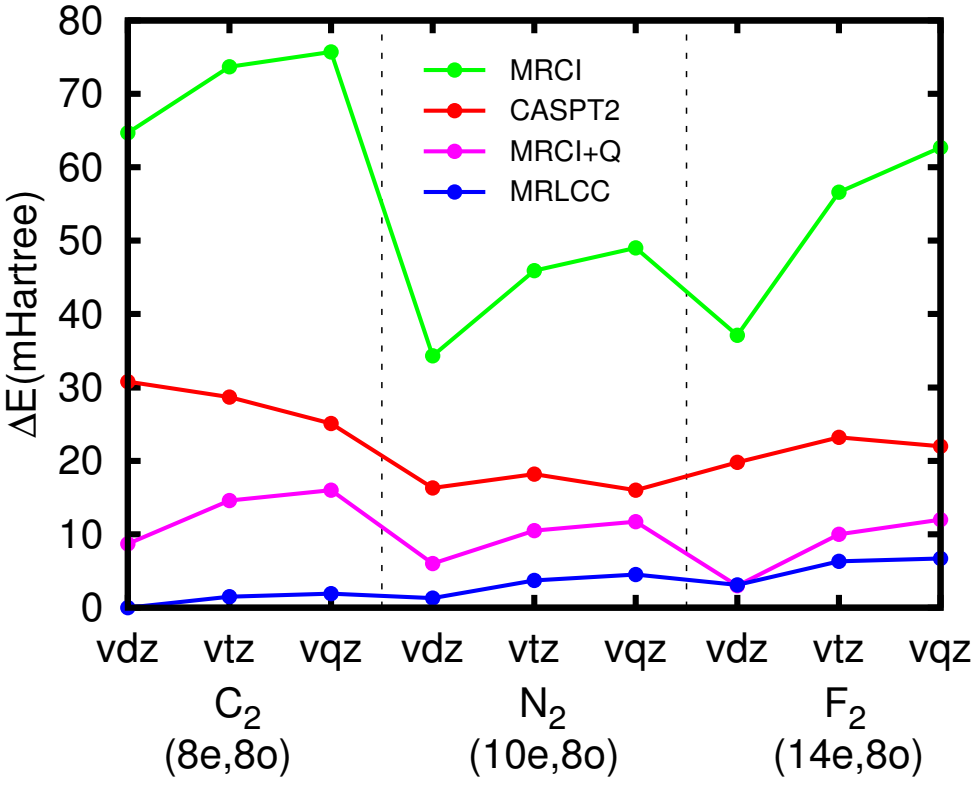
The truncated basis $b = \{\hat{E}_I |\Psi^{(0)}\rangle\}$ is used.

$$|\Psi^{(1)}\rangle = \sum_I \mathbf{d_I} \left(\hat{\mathbf{E}}_\mathbf{I} \sum_n c_n |D_n\rangle \right) = \sum_{I,n} \mathbf{d_I} c_n \left(\hat{\mathbf{E}}_\mathbf{I} |D_n\rangle \right)$$

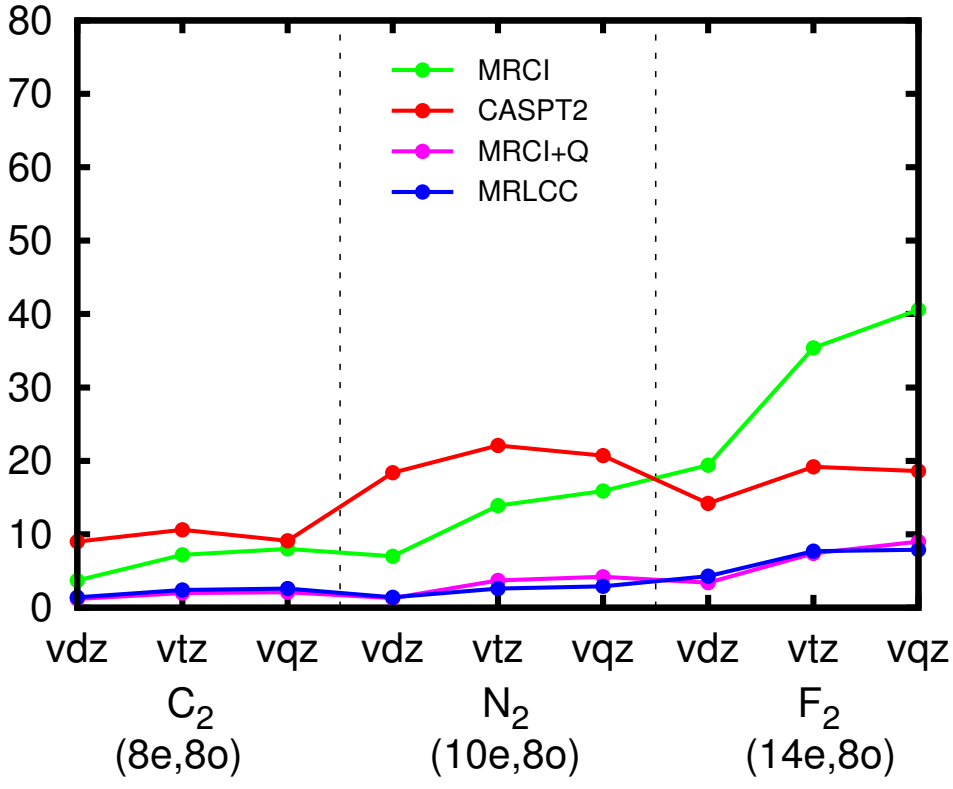
	FCI	uncontracted MRLCC2	contracted MRLCC2	Δ
Atomization Energy				
C_2	-0.207	-0.204	-0.204	0.000
N_2	-0.320	-0.314	-0.314	0.000
F_2	-0.044	-0.051	-0.051	0.000
Ionization Potential				
H_2O	-0.674	-0.674	-0.674	0.000
NH_3	-0.618	-0.612	-0.612	0.000
Cl_2		-0.411	-0.411	0.000
OH	-0.449	-0.470	-0.452	-0.018
Electron Affinity				
CH_3	-0.048	-0.049	-0.049	0.000
CN	0.100	0.100	0.100	0.000
NO	-0.053	-0.048	-0.048	0.000
SH		0.039	0.039	0.000

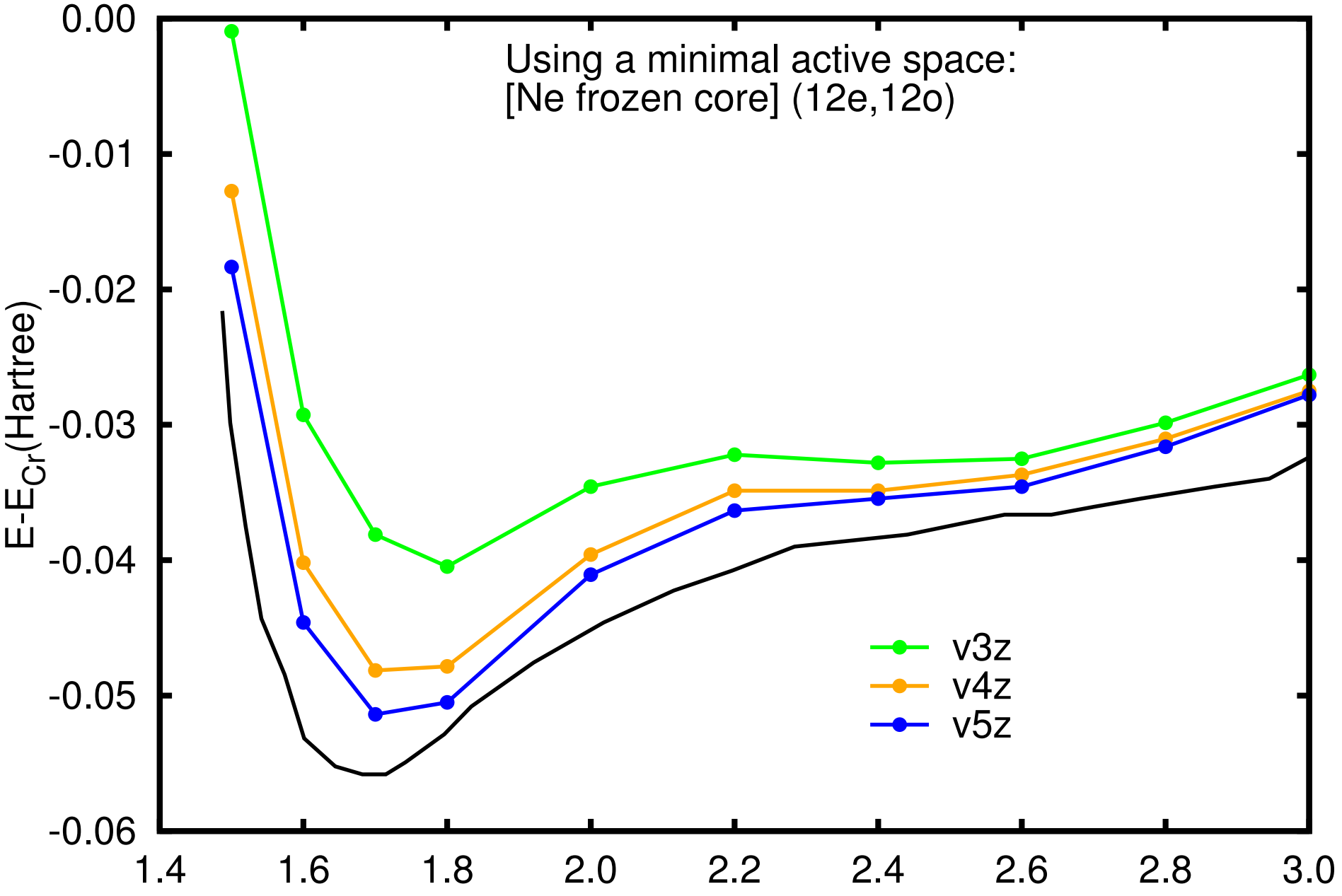

-75.60
-75.65
-75.70
-75.75
-75.80
E(Hartree)
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
NEVPT2
CASPT2
MRCI
MRLCC
FCI
ΔE(mHartree)
30
20
10
0
($\Psi^{(0)}$ is a frozen core (8,8) MCSCF)

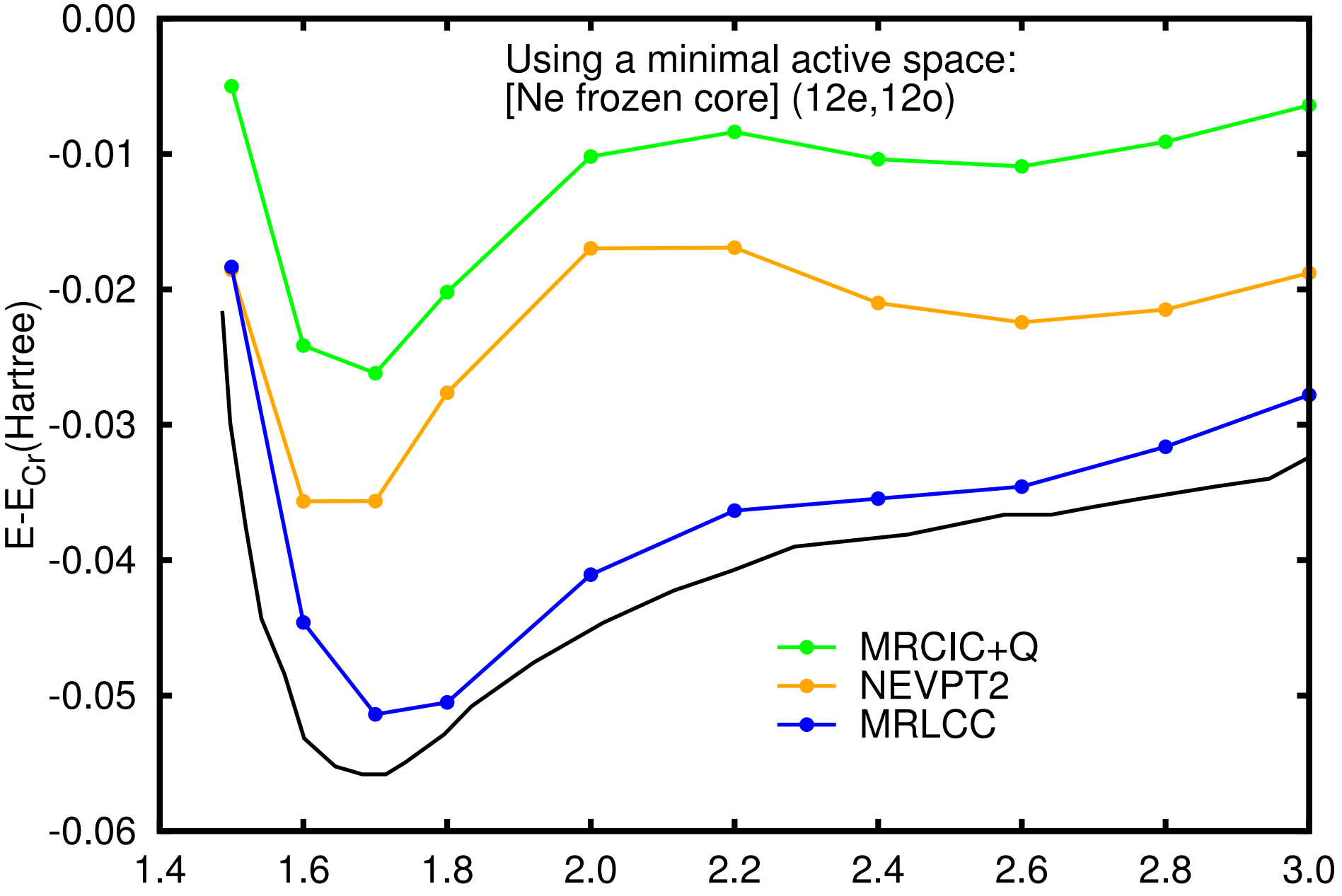
CAS-CI reference wavefunction



CASSCF reference wavefunction




Using a minimal active space:
[Ne frozen core] (12e,12o)
v3z
v4z
v5z
E-E$_{Cr}$(Hartree)
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
-0.06
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0


Using a minimal active space:
[Ne frozen core] (12e,12o)
MRCIC+Q
NEVPT2
MRLCC
E-E_Cr(Hartree)
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
-0.06
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0

We have a **DMRG+MRPT**/**HCI+MRPT** scheme involving zero-th order calculation with **extended active spaces** and a **fully internally contracted** perturbation theory, notably using the cheap and accurate **MRLCC** perturbation theory.

- **Third-order** $E^{(3)} = \sum_{IJK} d_I w_J d_K \left\langle \hat{E}_I^\dagger \hat{E}_J \hat{E}_K \right\rangle$
- **Density Fitting** $W_{pqrs} = \sum_{\mathbf{L}} (pr|\mathbf{L})\,(\mathbf{L}|qs)$
- **Cumulant approximation** $\mathrm{RDM}^{(k)} = \sum_{\sum \mathbf{i_n}=k} \left(\bigwedge \mathrm{RDM}^{(\mathbf{i_1})} \mathrm{RDM}^{(\mathbf{i_2})} \ldots \mathrm{RDM}^{(\mathbf{i_n})} \right)$
- **Cholesky decomposition** $\mathrm{RDM}^{(\mathbf{2n})}_{pqr\ldots uvw\ldots} = \sum_{\mathbf{L}} A^{(\mathbf{n})}_{pqr\ldots,\mathbf{L}} A^{(\mathbf{n})}_{\mathbf{L},uvw\ldots}$
- **Tensor contraction optimization**

Acknowledgments : Sandeep Sharma, Adam Holmes, James Smith

János G. Ángyán
1956 - 2017