

Multi-Reference Perturbation Theory using extended active space wavefunctions.

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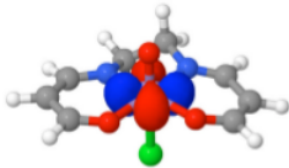
<https://mussard.github.io/>

Sandeep Sharma

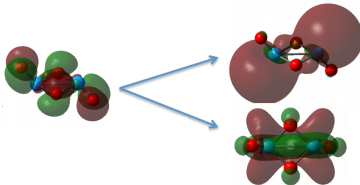
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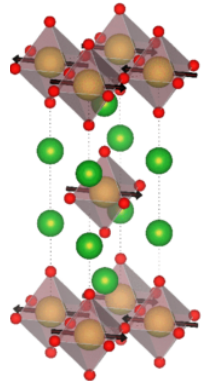
University of Colorado at Boulder



oxo-Mn Salen cluster



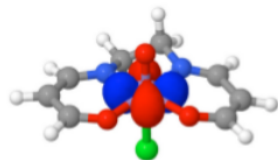
TiO₂ structure



Transition metal oxides

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, at least as accurate
- relative independance to the orbitals (versus MRCI)
- intruder state free (versus CASPT)

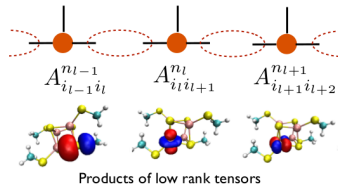
The bigger the **active space**, the more accurate the zero-th order wavefunction.

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 **very large active space**.

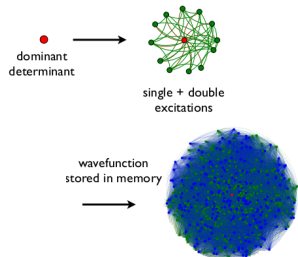
[Sharma, Chan JCP **136** (2012)]



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 wavefunction unto.

[Holmes, Tubman, Umrigar JCTC **12** (2016)]



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 :

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

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 $\hat{H}_{\text{Fink}} = (t_u^v \hat{E}_u^v + W_{uv}^{wx} \hat{E}_{uv}^{wx}) \Big|_{\Delta=0}$

[Sharma,Alavi JCP **143** (2015)]

[Fink CPL **428** (2006)]

 - **intruder state free**
 - **fairly independent of the reference calculation**

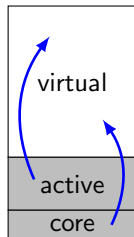
The first-order correction to the wavefunction $|\Psi^{(1)}\rangle$ lives in the **perturber space**, composed of all single and double excitations on all the determinants of the zero-th order wavefunction.

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.

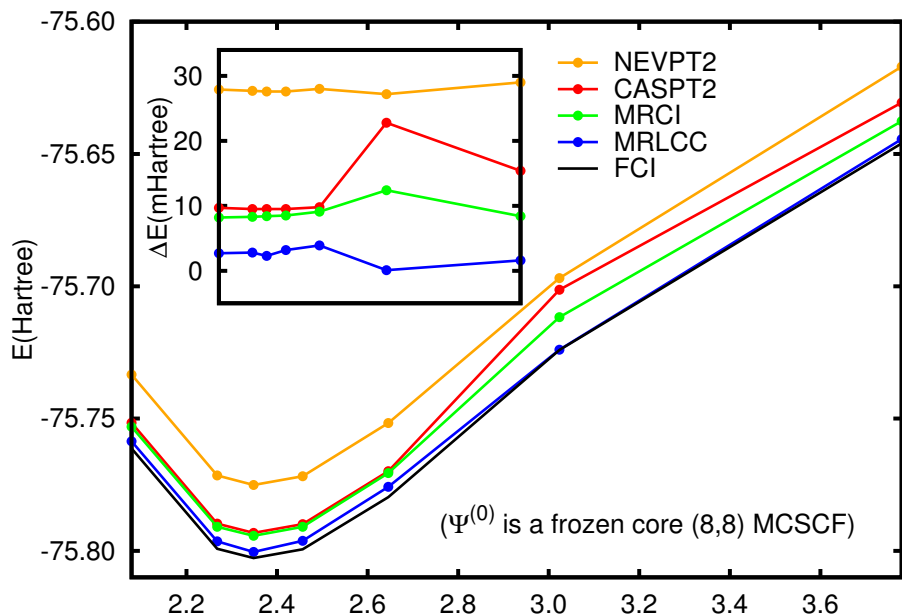
$$|\Psi^{(1)}\rangle = \sum_{c,I,n} \mathbf{d}_{In} \left(\hat{E}_I |D_n\rangle \right)$$

Internally contracted scheme

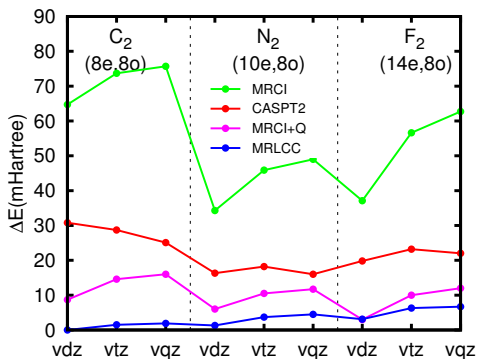
The truncated basis $b = \{\hat{E}_I |\Psi^{(0)}\rangle\}$ is used.

$$\begin{aligned} |\Psi^{(1)}\rangle &= \sum_{c,I} \mathbf{d}_I \left(\hat{E}_I \sum_n c_n |D_n\rangle \right) \\ &= \sum_{c,I,n} \mathbf{d}_I c_n \left(\hat{E}_I |D_n\rangle \right) \end{aligned}$$

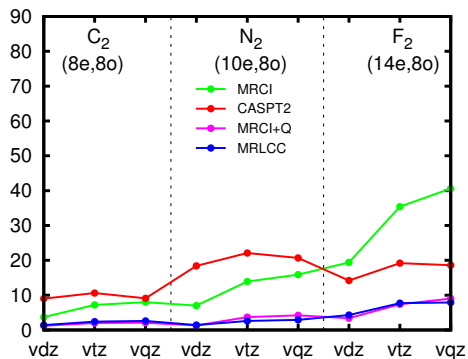
	FCI	uncontracted MRLCC2	contracted MRLCC2	Δ
Atomization Energy				
C ₂	-0.207	-0.204	-0.204	0.000
N ₂	-0.320	-0.314	-0.314	0.000
F ₂	-0.044	-0.051	-0.051	0.000
Ionization Potential				
H ₂ O	-0.674	-0.674	-0.674	0.000
NH ₃	-0.618	-0.612	-0.612	0.000
Cl ₂		-0.411	-0.411	0.000
OH	-0.449	-0.470	-0.452	-0.018
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

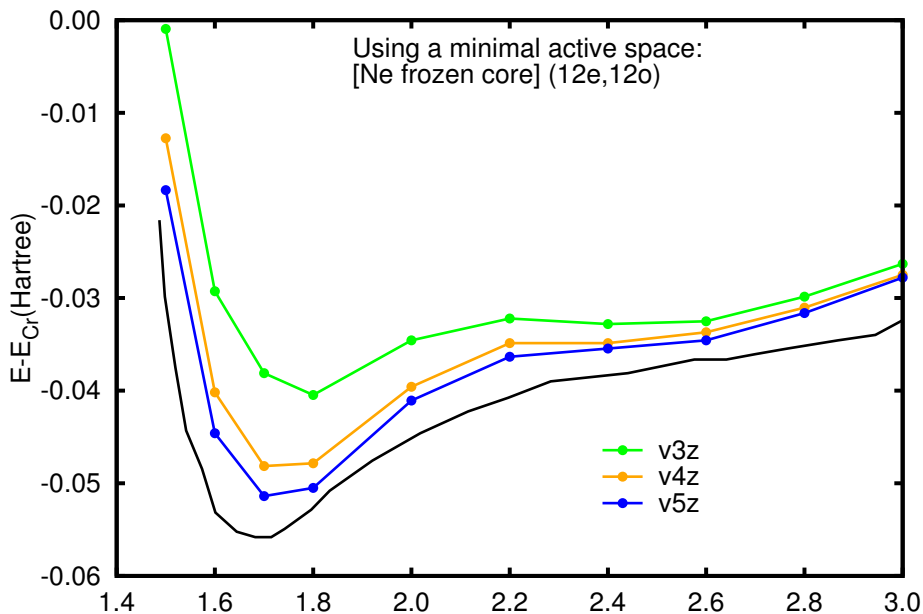


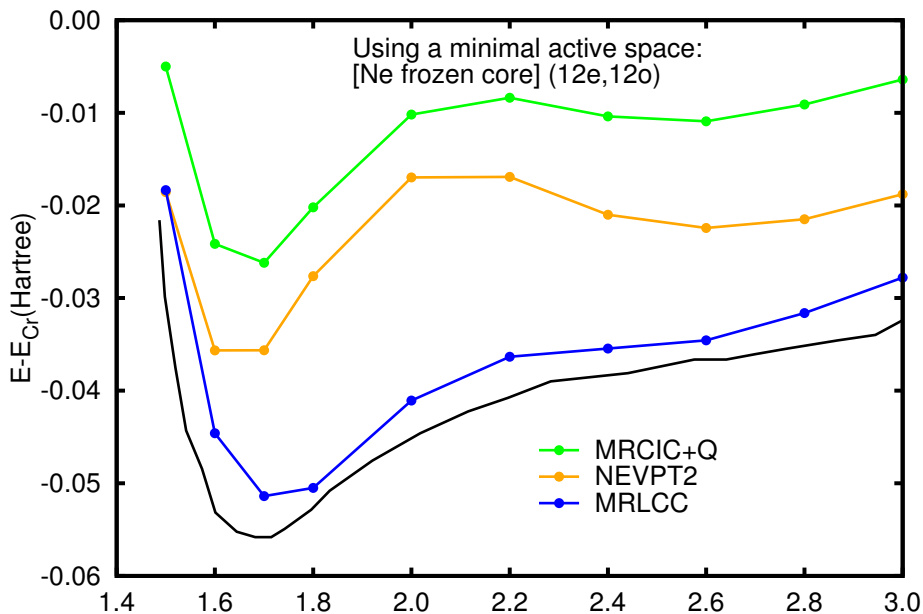
CAS-CI reference wavefunction



CASSCF reference wavefunction







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**

$$E^{(3)} = \sum_{IJK} d_I w_J d_K \langle \hat{E}_I^\dagger \hat{E}_J \hat{E}_K \rangle$$

- **Density Fitting**

$$W_{pqrs} = \sum_{\mathbf{L}} (pr|\mathbf{L})(\mathbf{L}|qs)$$

- **Cumulant approximation**

$$\text{RDM}^{(k)} = \sum_{\sum \mathbf{i}_n = k} \left(\bigwedge \text{RDM}^{(\mathbf{i}_1)} \text{RDM}^{(\mathbf{i}_2)} \dots \text{RDM}^{(\mathbf{i}_n)} \right)$$

- **Cholesky decomposition**

$$\text{RDM}_{pqr\dots uvw\dots}^{(2\mathbf{n})} = \sum_{\mathbf{L}} A_{pqr\dots, \mathbf{L}}^{(\mathbf{n})} A_{\mathbf{L}, uvw\dots}^{(\mathbf{n})}$$

- **Tensor contraction optimization**

Acknowledgments : Sandeep Sharma, Adam Holmes, James Smith



János G. Ángyán
1956 - 2017