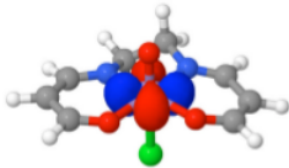


Multi-Reference Perturbation Theory

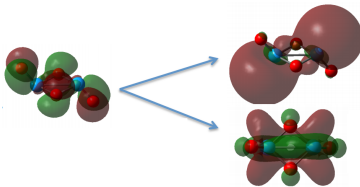
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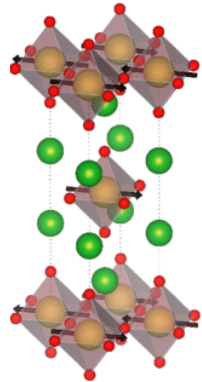
https://mussard.github.io/doc/talk_201704.pdf



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.

Strategies at our disposal are numerous.

- Orbitals ϕ , Slater determinants $|D\rangle$, wavefunctions $|\Psi\rangle$

- **The basics**

- (HF) Hartree-Fock approximation

- (FCI) Full Configuration Interaction

- **Single-reference methods** (Dynamical correlation)

- (CI) Configuration of Interaction

- (CC) Coupled-Cluster

- (PT) Perturbation Theory

- **Multi-reference methods** (Static correlation)

- (MCSCF) Multiconfigurational-SCF

- (CAS) Complete Active Space

- (**MRPT**) **Uncontracted scheme** v. **Internally contracted scheme**

- (another time ?) WFT+DFT hybrid methods

The aim : express the **wavefunction** $|\Psi\rangle = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$.

- Orbitals : basis of $\mathcal{L}^2(\mathbb{R}^3, \mathbb{C}) = \{f : \mathbb{R}^3 \rightarrow \mathbb{C} / f \text{ is square integrable}\}$

An **orbital** (ϕ) is a **wavefunction of a one-electron state**.

An infinite set $\{\phi\}_\infty$ of orbitals is a basis of $\mathcal{L}^2(\mathbb{R}^3, \mathbb{C})$.

A subset $\{\phi\}_{\mathbf{m}}$ is a basis of a subspace of $\mathcal{L}^2(\mathbb{R}^3, \mathbb{C})$.

- Determinants : basis of $\mathcal{A}^2(\mathbb{R}^{3N}, \mathbb{C}) = \{f \in \mathcal{L}^2(\mathbb{R}^{3N}, \mathbb{C}) / f \text{ is antisymmetric}\}$

A N -electrons **Slater determinant** ($|D\rangle$) is made from N given orbitals.

The infinite set $\{|D\rangle\}_\infty$ of all N -electron Slater determinants that can be made from a basis $\{\phi\}_\infty$ of $\mathcal{L}^2(\mathbb{R}^3, \mathbb{C})$ is a basis of $\mathcal{A}^2(\mathbb{R}^{3N}, \mathbb{C})$.

A subset $\{|D\rangle\}_{\mathbf{m}}$ is a basis of a subspace of $\mathcal{A}^2(\mathbb{R}^{3N}, \mathbb{C})$.

$|\Psi\rangle \in \mathcal{A}^2(\mathbb{R}^{3N}, \mathbb{C})$, so it is approximated in the basis $\{|D\rangle\}_{\mathbf{m}}$: $|\Psi\rangle = \sum c_I |D_I\rangle$

- **Full Configuration Interaction (FCI)** → **all determinants**

$$|\Psi_{\text{FCI}}\rangle = \sum_I \mathbf{c}_I |D_I\rangle \quad \text{and}$$

$$E_{\text{FCI}} = \min_{\{\mathbf{c}_I\}} \langle \Psi_{\text{FCI}} | \hat{H} | \Psi_{\text{FCI}} \rangle$$

This corresponds to diagonalizing the Hamiltonian in the space of all determinants.

- **Hartree-Fock approximation (HF)** → **only one determinant**

$$|\Psi_{\text{HF}}\rangle = |D_0(\{\phi_i\})\rangle \quad \text{and}$$

$$E_{\text{HF}} = \min_{\{\phi_i\}} \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle$$

The determinants $|D_I\rangle$ are labelled wrt. the HF determinant :

$$|D_I\rangle = \hat{E}_I |D_0\rangle \quad (\text{excitations or configurations})$$

The **correlation energy** is what is missing in HF with respect to the exact energy.

ϕ_m	unocc.
\vdots	(in $ D_0\rangle$)
\vdots	<i>virtual</i>
ϕ	
$\overline{\phi_N}$	occupied
\dots	(in $ D_0\rangle$)
ϕ_1	

Situations where for all I , $c_I \ll c_0$

Those are situations where the **HF determinant is a good starting point** for the exact wavefunction : one can consider “**single-reference post-HF methods**”.

These are approximations to $|\Psi_{\text{FCI}}\rangle$ that assume the predominance of $|D_0\rangle$.

This arises in systems with a large HF gap (H_2 at equilibrium).

- Configuration of Interaction (CI)

$$|\Psi_{\text{CI}}\rangle = \sum_{I \in \text{sub}} c_I \hat{\mathbf{E}}_I |D_0\rangle \quad \rightarrow \quad \text{truncated FCI, } \underline{\text{less determinants than FCI}}$$

- Coupled-Cluster (CC)

$$|\Psi_{\text{CC}}\rangle = e^{t_I \hat{\mathbf{E}}_I} |D_0\rangle \quad \rightarrow \quad \text{all the determinants of the FCI, but } \underline{\text{less parameters}}$$

CC can be seen as an effort to reduce the size of the parameter space of FCI

- Perturbation Theory (PT)

$$\hat{H} = \hat{H}_0 + \hat{\mathbf{V}} \quad \rightarrow \quad \text{is not guaranteed to converge}$$

$$\hat{H}_0 |D_0\rangle = E^{(0)} |D_0\rangle$$

Situations where for some I , $\mathbf{c}_I \sim \mathbf{c}_0$

Those are situations where the **HF determinant is NOT a good starting point** for the exact wavefunction.

Single-ref. methods would give too much importance to $|D_0\rangle$.

This arises in systems with a small HF gap (H_2 at dissociation).

- **Multiconfigurational-SCF (MCSCF)** (a **multideterminantal extension to HF**)

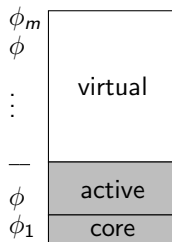
$$|\Psi_{\text{MCSCF}}\rangle = \sum_n \mathbf{c}_n |D_n\rangle \quad \text{and}$$

$$E_{\text{MCSCF}} = \min_{\{\mathbf{c}_n, \phi_i\}} \langle \Psi_{\text{MCSCF}} | \hat{H} | \Psi_{\text{MCSCF}} \rangle$$

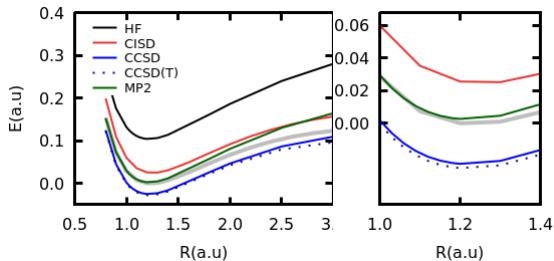
- **Complete Active Space (CAS)**

Includes all determinants that can be generated from an orbital subspace. (This is a FCI in this subspace).

The “out-of-active space” dynamical correlation is untreated, and one can use “**multi-reference post-MCSCF methods**” (such as MRCI, MRCC, **MRPT**, ...)



Single-reference methods



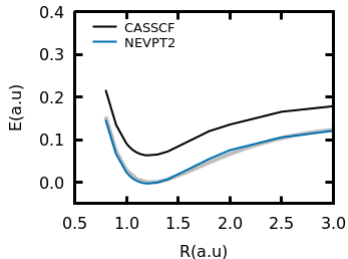
-**HF** : no correlation (by def.)

-**CISD** is variational
It recovers part of the **dynam. correlation**

-**CCSD(T)** is not variational
It is considered the “gold standard”

-**MP2** : often surprisingly good

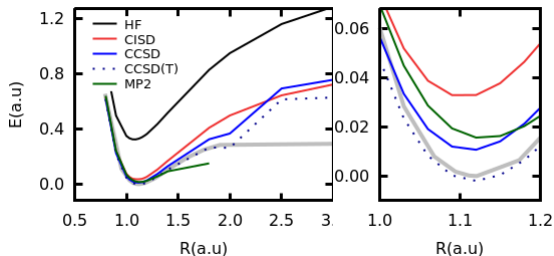
Multi-reference methods



-**CASSCF** recovers the **static correlation**

-**MRPT** is **almost exact**

Single-reference methods



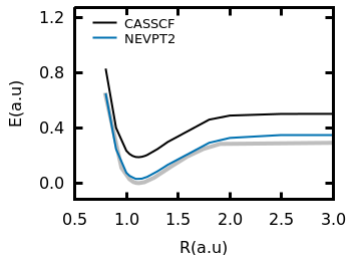
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Multi-reference methods



-**CASSCF** recovers the **static correlation**

-**MRPT** is **almost exact**

- We are doing Rayleigh-Schrödinger PT and want 2nd- and 3rd-order corrections :

$$E^{(2)} = \langle \Psi^{(0)} | \hat{V} | \Psi^{(1)} \rangle \quad E^{(3)} = \langle \Psi^{(1)} | \hat{V} - E^{(1)} | \Psi^{(1)} \rangle$$

- We express $|\Psi^{(1)}\rangle$ in a basis of “perturber wavefunctions” $b = \{|B\rangle\}$ and solve :

$$(E^{(0)} - \hat{H}_0) |\Psi^{(1)}\rangle = \hat{V} |\Psi^{(0)}\rangle \quad \Leftrightarrow \quad \sum_J \underbrace{\langle B_I | (E^{(0)} - \hat{H}_0) | B_J \rangle}_{A_{IJ}} \mathbf{d}_J = \underbrace{\langle B_I | \hat{V} | \Psi^{(0)} \rangle}_{S_I}$$

$$\left[\begin{array}{l} \text{In the single-reference case the determination of } |\Psi^{(1)}\rangle \text{ is not an issue.} \\ \text{The basis } b = \{|\Psi_I^{(0)}\rangle\} \text{ is composed of the eigenvectors of } \hat{H}_0 \text{ that are not } |\Psi^{(0)}\rangle : \\ \mathbf{d}_I = \frac{\langle \Psi_I^{(0)} | \hat{V} | \Psi^{(0)} \rangle}{E^{(0)} - E_I^{(0)}} \quad E^{(2)} = \langle \Psi^{(0)} | \hat{V} \left[\frac{\langle \Psi_I^{(0)} | \hat{V} | \Psi^{(0)} \rangle}{E^{(0)} - E_I^{(0)}} \right] | \Psi_I^{(0)} \rangle \end{array} \right]$$

In multi-reference PT it would entail **inverting in a many-body space**.

- Any wavefunction of **the space outside the CAS** (connected to a determinant of the zero-th order wavefunction) is a perturber wavefunction.

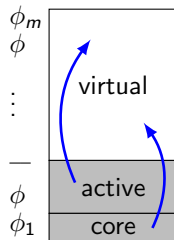
- The **zero-th order wavefunction** reads :

$$|\Psi^{(0)}\rangle = \sum c_n |D_n\rangle = \sum c_n |D^c D_n^a D^v\rangle$$

- A **perturber wavefunction** (labelled μ) will be of the form :

$$|\Psi_{\mu}^{c'a'v'}\rangle = \sum c_{\mu,l}^{c'a'v'} |D^{c'} D_l^{a'} D^{v'}\rangle$$

$$\text{with : } |D^{c'} D_l^{a'} D^{v'}\rangle = \hat{E}_{l,n}^{c'a'v'} |D_n\rangle$$



In other words the perturber wavefunctions belong to the space $S = \bigoplus S^{(c)}$ where the spaces $S^{(c)}$ are spanned by the basis :

$$b^{(c)} = \{\hat{E}_{l,n}^{(c)} |D_n\rangle\} \quad (c) = (c' a' v')$$

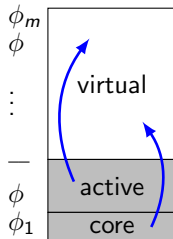
- All the objects interesting in this context are decomposed this way :

$$|\Psi^{(1)}\rangle = \sum |\Psi^{(1,c)}\rangle, \quad \hat{V} = \sum \hat{V}^{(c)}, \quad E_2 = \sum E_2^{(c)}, \quad \text{etc...}$$

The space $S^{(c)}$ is generated by **two-electron operators** $\hat{E}_{l,n}^{(c)}$.

The action of a two-electron operator on an object made of orbitals separated into core, active and virtual orbitals can be separated into **8 classes of excitations** in terms of the changes of the occupation pattern.

	Names		c'	a'	v'	Operators
I	CCVV	$V_{ij,ab}^{(0)}$	-2	0	+2	$\hat{E}_{l,n}^{(c)} \rightarrow \hat{E}_i^a \hat{E}_j^b$
II	ACVV	$V_{i,ab}^{(-1)}$	-1	-1	+2	$\hat{E}_{l,n}^{(c)} \rightarrow \hat{E}_i^a \hat{E}_r^b$
III	CAAV	$V_{ij,a}^{(+1)}$	-2	+1	+1	$\hat{E}_{l,n}^{(c)} \rightarrow \hat{E}_i^a \hat{E}_j^r$
IV	AAVV	$V_{ab}^{(-2)}$	0	-2	+2	$\hat{E}_{l,n}^{(c)} \rightarrow \hat{E}_r^a \hat{E}_s^b$
V	CCAA	$V_{ij}^{(+2)}$	-2	+2	0	$\hat{E}_{l,n}^{(c)} \rightarrow \hat{E}_i^r \hat{E}_j^s$
VI	CAAV	$V_{i,a}^{(0)}$	-1	0	+1	$\hat{E}_{l,n}^{(c)} \rightarrow \hat{E}_i^a \hat{E}_s^r, \hat{E}_s^a \hat{E}_i^r$
VIII	AAAV	$V_a^{(-1)}$	0	-1	+1	$\hat{E}_{l,n}^{(c)} \rightarrow \hat{E}_s^r \hat{E}_a^r$
VII	AAAC	$V_i^{(+1)}$	-1	+1	0	$\hat{E}_{l,n}^{(c)} \rightarrow \hat{E}_t^r \hat{E}_j^s$



- Uncontracted scheme

$|\Psi^{(1,c)}\rangle$ is written in the basis $b_{UC}^{(c)} = b^{(c)} = \{\hat{E}_{l,n}^{(c)} | D_n \rangle\}$ of all possible double excitations to all the determinants composing $|\Psi^{(0)}\rangle$:

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

[The class $\hat{E}_{l,\mathbf{n}}^{(c)} = \hat{E}_r^a \hat{E}_s^b$ (two actives to two virtuals) has $O(N_{\text{act.}} N_{\text{vir.}} \mathbf{N}_{\text{det.}})$ coef.]

- Contracted scheme

Another option is to consider the truncated basis $b_C^{(c)} = \{\hat{E}_l^{(c)} | \Psi^{(0)} \rangle\}$:

$$|\Psi^{(1,c)}\rangle = \sum_l \mathbf{d}_l^{(c)} \left(\hat{\mathbf{E}}_l^{(c)} \sum_n c_n | D_n \rangle \right)$$

This is a factorization (much like CC is a factorization of the parameters of FCI) and you could get (approximation to) the original coefficients : $d_{l,n}^{(c)} \approx d_l^{(c)}.c_n$.

[The class $\hat{E}_l^{(c)} = \hat{E}_r^a \hat{E}_s^b$ (two actives to two virtuals) has $O(N_{\text{act.}} N_{\text{vir.}})$ coefficients.]

	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

The engine : The coefficients **d** are found by solving **Ad = s** (for each class) :

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

$$s_I = \langle B_I | \hat{V} | \Psi^{(0)} \rangle = \sum \langle \Psi^{(0)} | \hat{E}_I^\dagger \hat{E}_J | \Psi^{(0)} \rangle w_J$$

- The terms (like $\langle \Psi^{(0)} | \hat{E}_I^\dagger \hat{H}_0 \hat{E}_J | \Psi^{(0)} \rangle$) are fed to a Python library (sqa) that returns **tensor contractions of 1- and 2-electrons integrals and RDMs** :

$$\left[\begin{array}{llll} \text{Ad}[\text{abcd}] & = & -2.0 \text{ f}[\text{ce}] & \text{d}[\text{abde}] \\ \text{Ad}[\text{abcd}] & = & 4.0 \text{ W}[\text{cdef}] & \text{d}[\text{abef}] \\ \text{Ad}[\text{abcd}] & = & -2.0 \text{ f}[\text{ce}] \text{ E1}[\text{fd}] & \text{d}[\text{abef}] \\ \text{Ad}[\text{abcd}] & = & 1.0 \text{ W}[\text{cdef}] \text{ E1}[\text{ge}] & \text{d}[\text{abfg}] \\ \text{Ad}[\text{abcd}] & = & 1.0 \text{ f}[\text{ef}] \text{ E2}[\text{fgcd}] & \text{d}[\text{abeg}] \\ \text{Ad}[\text{abcd}] & = & -2.0 \text{ W}[\text{cefg}] \text{ E2}[\text{ehgd}] & \text{d}[\text{abfh}] \\ \text{Ad}[\text{abcd}] & = & 1.0 \text{ W}[\text{efgh}] \text{ E3}[\text{fghi cd}] & \text{d}[\text{abe i}] \end{array} \right]$$

- These tensor contraction informations are read and performed by a C++ program (icpt) that computes **d** by conjugate-gradient.
- All this is interfaced into the widely-used Python program PySCF.

- Fully internally contracted

- Third-order

$$\begin{aligned} E^{(3)} &= \sum_{c_1 c_2 c_{12}} \langle \Psi_1^{(c_1)} | \hat{V}^{(c_{12})} | \Psi_1^{(c_2)} \rangle \\ &= \sum_{c_1 c_2 c_{12}} \sum_{IJK} d_I^{(c_1)} w_J^{(c_{12})} d_K^{(c_2)} \langle \hat{E}_I^{(c_1)\dagger} \hat{E}_J^{(c_{12})} \hat{E}_K^{(c_2)} \rangle \end{aligned}$$

- 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

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

- Tensor contraction optimization

- (mid- to long-term project) F12 addition and Range-separation

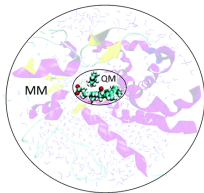
$$\hat{W}_{ee} = \lambda \hat{W}_{ee} + (1 - \lambda) \hat{W}_{ee}$$

$$E = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ne} + \lambda \hat{W}_{ee} | \Psi \rangle + \bar{E}_{\text{Hxc}}^{\text{DFT}, \lambda} [n_{\Psi}] \right\}$$

A closer look :

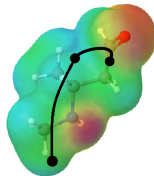
QM/MM :

“Real space region”
different treatment



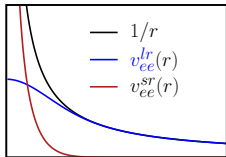
Hybrid method :

$$\lambda \underset{\uparrow \text{WFT}}{\hat{W}_{ee}} + (1 - \lambda) \underset{\uparrow \text{DFT}}{\hat{W}_{ee}} (= \hat{W}_{ee})$$



$$\hat{W}_{ee} = \hat{W}_{ee}^{\text{lr}} + \hat{W}_{ee}^{\text{sr}}$$

$$E = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{DFT}, \text{sr}} [n_{\Psi}] \right\}$$



Range-separation :

$$\underset{\uparrow \text{WFT}}{\hat{W}_{ee}^{\text{lr}}} + \underset{\uparrow \text{DFT}}{\hat{W}_{ee}^{\text{sr}}} (= \hat{W}_{ee})$$

