Tensorized orbitals for computational chemistry

Workshop on tensor networks - October 9th, 2025 - Grenoble

- N. Jolly, Y.N. Fernández, X. Waintal, *Tensorized orbitals for computational chemistry*, Phys. Rev. B. **111** (2025) 245115.
- Additional works (yet non-published)

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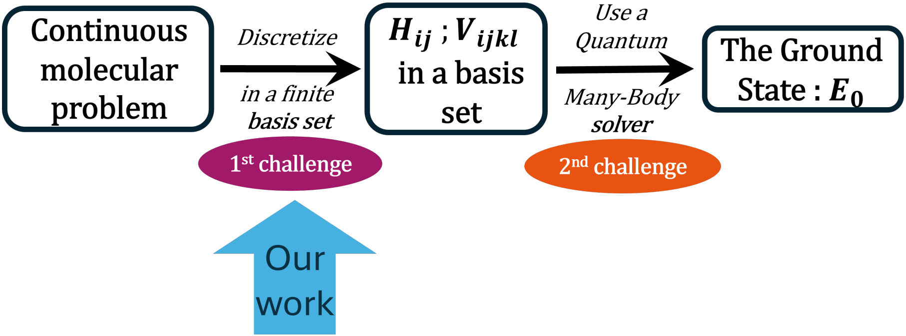
General overview



Our goal

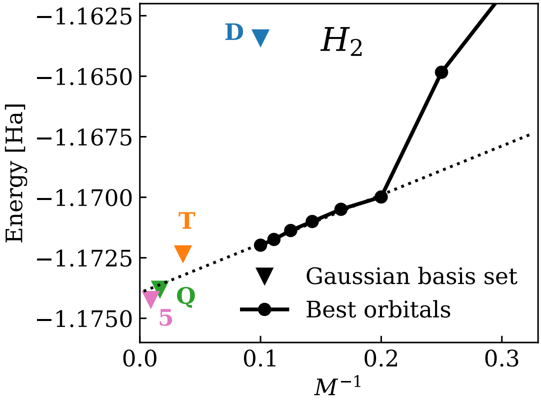


Figure: H_2 energy for different basis sets.
The **best orbitals** get the accuracy of the T at the price of the D

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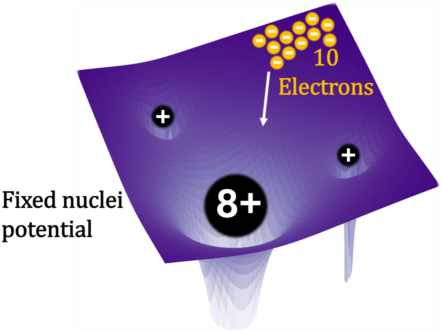
The quantum chemistry problem

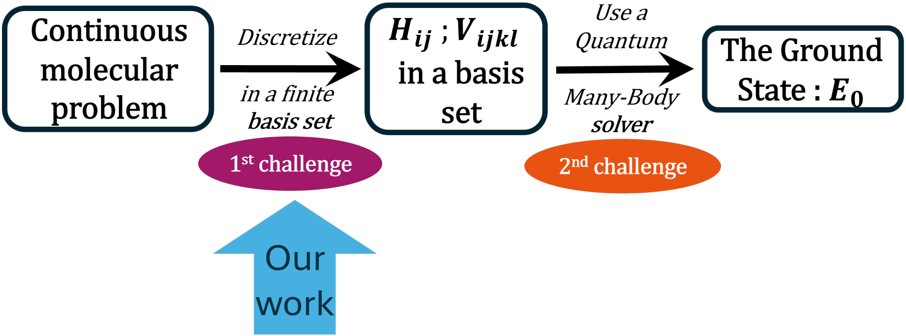
Example : H_2O molecule



Input : Fixed nuclei positions

Output : Ground state energy

General overview



The quantum chemistry hamiltonian

Molecular hamiltonian, nuclei of charge Z_α positioned at $\vec{R}_\alpha$

In the proper unit system, the hamiltonian of the electrons is :

$$\hat{\mathcal{H}} = -\sum_{\sigma} \int d\vec{r}\Psi^\dagger_\sigma(\vec{r})\frac{\Delta}{2}\Psi_\sigma(\vec{r}) - \sum_{\sigma,\alpha} \int d\vec{r} Z_\alpha \frac{\Psi^\dagger_\sigma(\vec{r})\Psi_\sigma(\vec{r})}{|\vec{r}-\vec{R}_\alpha|} + \sum_{\sigma\sigma'} \int d\vec{r}d\vec{r}' \frac{\Psi^\dagger_\sigma(\vec{r})\Psi_\sigma(\vec{r})\Psi^\dagger_{\sigma'}(\vec{r}')\,\Psi_{\sigma'}(\vec{r}')}{|\vec{r}-\vec{r}'|} \tag{1}$$

Given a *basis set* of orbitals $\Phi = \{\phi_i\}_{i=1\ldots M}$ and with $c^\dagger_{i\sigma} = \int d\vec{r}\ \phi_i(\vec{r})\Psi^\dagger_\sigma(\vec{r})$:

$$\hat{\mathcal{H}} = \sum_{ij\sigma} H_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \sum_{ijkl\sigma\sigma'} V_{ijk\ell} c^\dagger_{i\sigma} c^\dagger_{j\sigma'} c_{k\sigma'} c_{\ell\sigma} \tag{2}$$

Then, the problem is characterized by :

$$\begin{aligned} H_{ij} &= -\int d\vec{r}\ \frac{\phi_i(\vec{r})\Delta\phi_j(\vec{r})}{2} - \int d\vec{r}\ \sum_\alpha \frac{Z_\alpha\phi_i(\vec{r})\phi_j(\vec{r})}{|\vec{r}-\vec{R}_\alpha|} \\ V_{ijk\ell} &= \int d\vec{r}_1 d\vec{r}_2\ \frac{\phi_i(\vec{r}_1)\phi_j(\vec{r}_1)\cdot\phi_k(\vec{r}_2)\phi_\ell(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|} \end{aligned} \tag{3}$$

Units and orders of magnitude

Units: Distances are in *Bohr Radius* : $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{2m_e} \approx 0.5\mathring{A}$

Energies are in *Hartree* $1\ \mathrm{Ha} = E_h = \hbar c\alpha/a_0 = 27.2\mathrm{eV} \approx 30\ 000\mathrm{K}$

Orders of magnitude: $H_{ij}, V_{ijk\ell}$ can be as high as $10 - 100\mathrm{Ha}$

Chemical accuracy : $1\mathrm{mHa} = 300K$

Biological accuracy : $\ll 10\mu\mathrm{Ha} = 3K$??

Limits of gaussians

The standard resolution methods only use **Gaussian-based** orbitals, defined as :

$$\psi^{\text{gaussian}}(\vec{r}) = \sum_i \alpha_i e^{-\frac{r^2}{\zeta_i^2}} \tag{4}$$

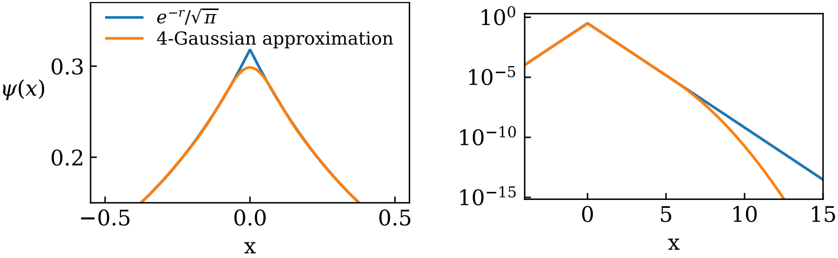


Figure: Exact 1s orbital of Hydrogen VS Approximation with 4 gaussians

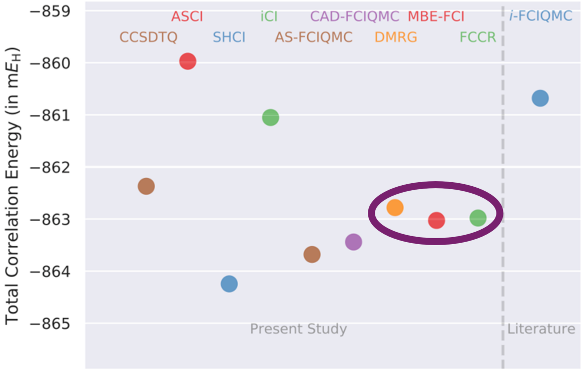
Precision is not accuracy

Once discretized, we need a **solver :**

Figure: Benzene, with `cc-pvDz` (30 electrons, 108 orbitals)

Precision is not accuracy

Once discretized, we need a **solver** :



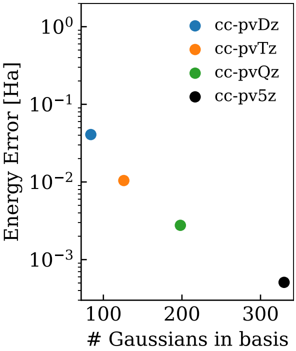
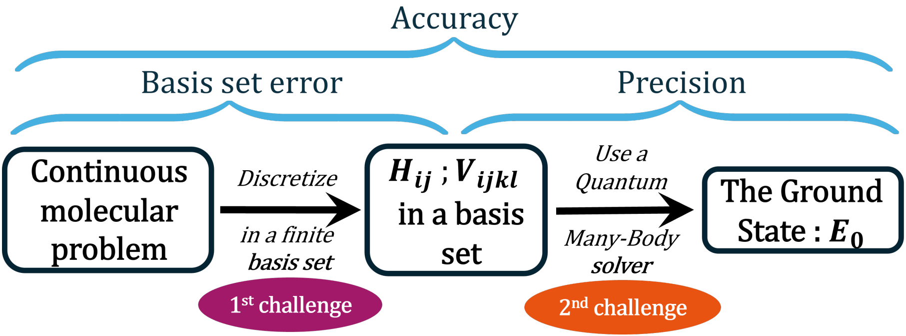


Figure: Benzene, with `cc-pvDz` (30 electrons, 108 orbitals)

$\Longrightarrow$ With such a basis set, **precision** is not **accuracy**

General overview



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Quantics

Discretization onto exponentially fine grid

We use *Quantics* to describe continuous functions in 3D :

$$\vec{r} \in [-50, 50]^3 \quad \Longrightarrow \quad x_1 x_2 \cdots x_n \; y_1 \cdots y_n \; z_1 \cdots z_n, \quad x_i, y_i, z_i \in \{0, 1\}$$

$$\text{With : } \vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = -50 + 50 \cdot \begin{pmatrix} \frac{x_1}{2^1} + \frac{x_2}{2^2} + \cdots + \frac{x_n}{2^n} \\ \frac{y_1}{2^1} + \frac{y_2}{2^2} + \cdots + \frac{y_n}{2^n} \\ \frac{z_1}{2^1} + \frac{z_2}{2^2} + \cdots + \frac{z_n}{2^n} \end{pmatrix} \tag{5}$$

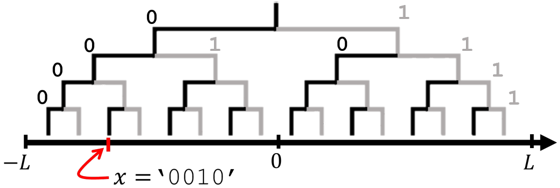


Figure: The positions are mapped to their coordinate in this tree

Interpolation accuracy

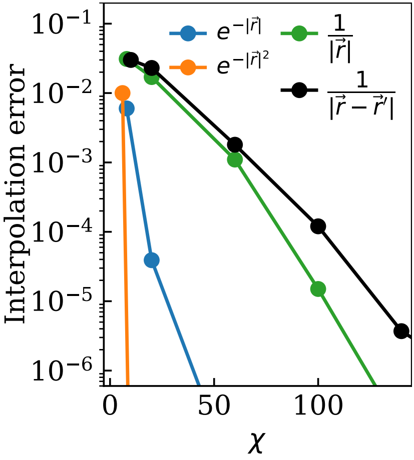
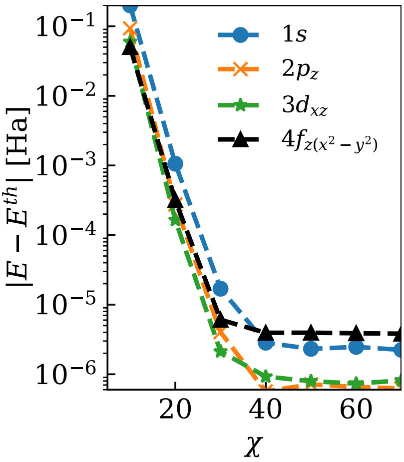


Figure: The relevant functions are **interpolated accurately** with the Tensor Cross Interpolation algorithm (TCI)

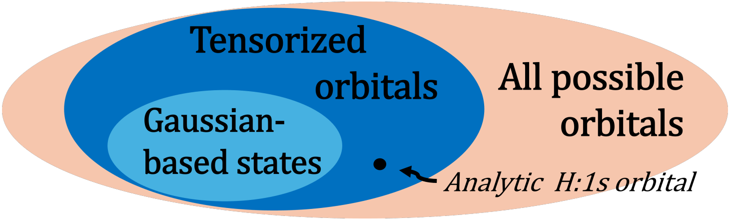
Physical accuracy

Figure: The interpolations are **physically precise** : they give out accurate energy !

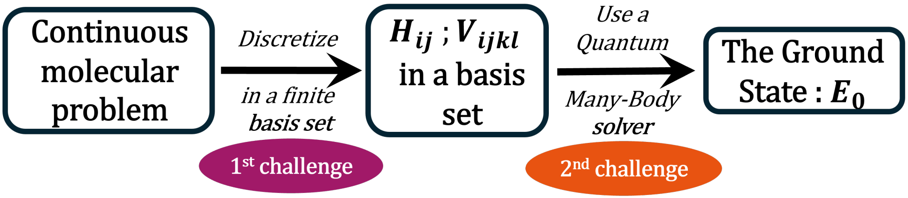


Tensorized orbitals

Conclusion: MPSs considerably expand the set of usable functions.



General overview



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Integrals to compute

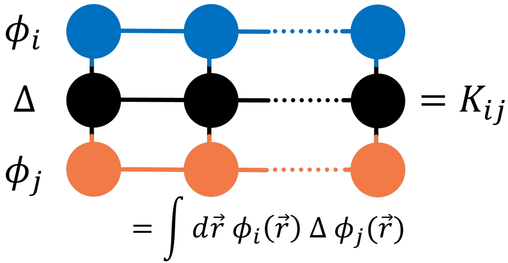
We saw that the problem is completely determined by these 4 objects :

$$
\begin{aligned}
S_{ij} &= \int d\vec{r}\ \varphi_i(\vec{r})\varphi_j(\vec{r}) \\
K_{ij} &= -\int d\vec{r}\ \frac{\varphi_i(\vec{r})\Delta\varphi_j(\vec{r})}{2} \\
P_{ij}^{\alpha} &= -\int d\vec{r}\frac{Z_\alpha\varphi_i(\vec{r})\varphi_j(\vec{r})}{|\vec{r}-\vec{R}_\alpha|} \\
V_{ijk\ell} &= \int d\vec{r}_1 d\vec{r}_2\ \frac{\varphi_i(\vec{r}_1)\varphi_j(\vec{r}_1)\cdot\varphi_k(\vec{r}_2)\varphi_\ell(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}
\end{aligned}
\tag{6}
$$

$\Longrightarrow$ We compute them by QTT contractions

The simple ones

The S_{ij}, K_{ij}, P_{ij}^{α} are computed using standard MPS/MPO operations. For example, K_{ij} :



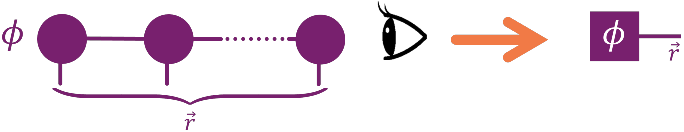
MPS-MPO-MPS contraction

Very fast compared to the other operations, because $\chi_\Delta = 4$

The crux : first getting the product orbitals

First, we compute $\phi_{ij}(\vec{r}) = \phi_i(\vec{r})\phi_j(\vec{r})$, **the product orbitals**.

Side view representation :



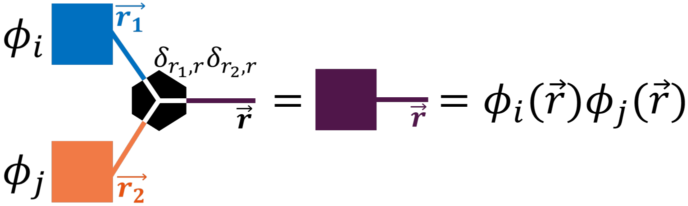
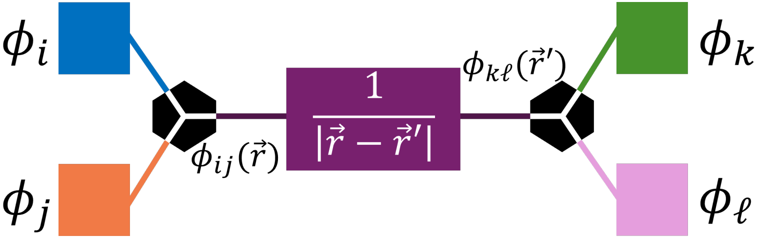


Figure: **Element-wise multiplication** [side view]

and finally computing the $V_{ijk\ell}$



$$= \iint d\vec{r}\, d\vec{r}' \, \frac{\phi_i(\vec{r})\phi_j(\vec{r}) \cdot \phi_k(\vec{r}')\phi_\ell(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

Figure: $V_{ijk\ell}$ computation, as MPS-MPO-MPS contraction of product orbitals [side view]

Proof of concept : *LiH* with `sto-6g` basis set

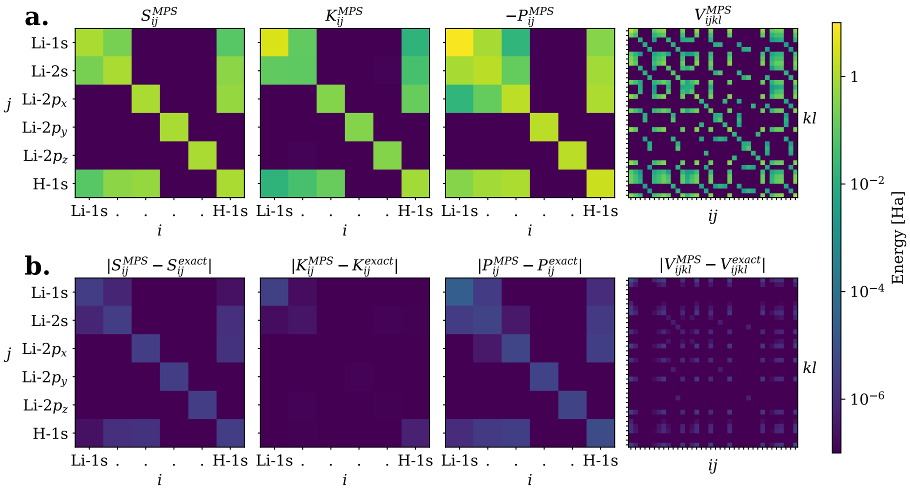
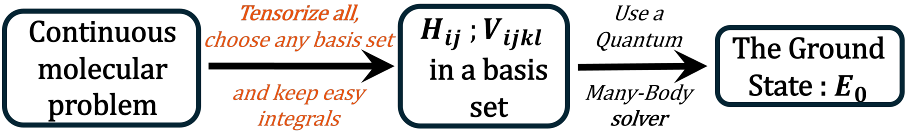


Figure: For a gaussian basis set (`sto-6g`), we compare the exact computations with a chemistry package (`Pyscf`) and the QTT computations.

Proof of concept : LiH with `sto-6g` basis set



Note on ordering and discretization

Grouped ordering :

$$\vec{r} \Longrightarrow x_1 x_2 \cdots x_n \; y_1 \cdots y_n \; z_1 \cdots z_n$$

Interlaced ordering :

$$\vec{r} \Longrightarrow x_1 y_1 z_1 \; x_2 y_2 z_2 \; \cdots \; x_n y_n z_n$$

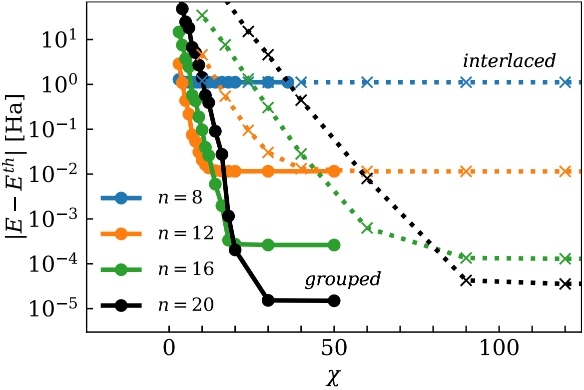


Figure: Accuracy of the "*LiH* with `sto-6g`" calculation as function of rank χ
Effect of **bit ordering** and grid density

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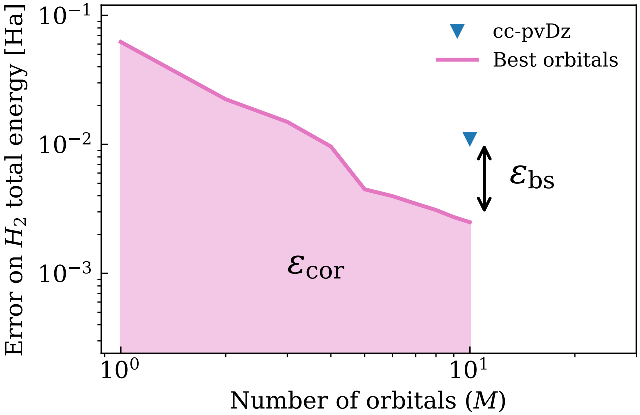
The initial insight

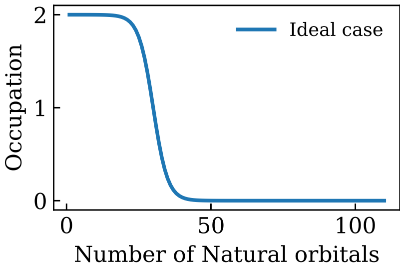


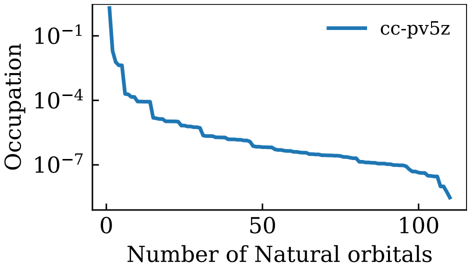
The error $\epsilon_{\text{basis set}}$ is only due to a **poor quality basis set**.
The error ϵ_{corr} occurs because we are **limited by the number of orbitals** to properly describe the correlations.

Natural orbitals

1-body density matrix

Once we found the ground state, we get the 1-body density matrix $\gamma_{ij} = \left\langle c_i^\dagger c_j \right\rangle$
The eigenstates are **optimally occupied orbitals**, the eigenvalues are the occupation numbers.
These are the **Natural Orbitals**.





$\Longrightarrow$ We can then move to the basis of natural orbitals : $\psi_\alpha = \Lambda_{\alpha i}\phi_i$

The enrichment process

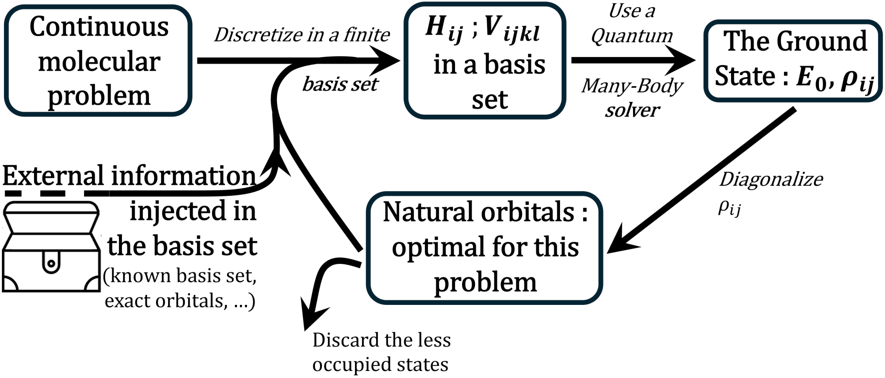


Figure: **Enrichment algorithm**, iteratively extracting from known orbitals, the overall bests for the given problem

Simulation results

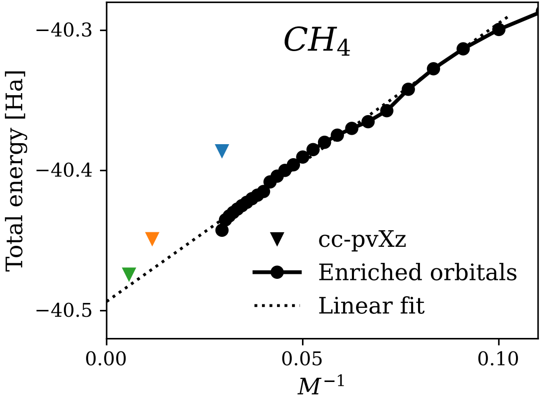


Figure: Methane energy with a basis set of size $M = 34$.
The enrichment is done over the cc−pv5z basis set (having 311 orbitals).

Computing the gradient

Energy functionnal

Once we solved for the density matrices $\gamma_{ij} = \left\langle c_i^\dagger c_j \right\rangle$ and $\gamma_{ijk\ell} = \left\langle c_i^\dagger c_k^\dagger c_j c_\ell \right\rangle$, the **energy** is :

$$E[\Phi] = \gamma_{ij} \int d\vec{r} \phi_i \left[-\Delta_{\vec{r}} - \frac{Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} \right] \phi_j + \gamma_{ijk\ell} \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\phi_i \phi_j(\vec{r}) \phi_k \phi_l(\vec{r}')}{|\vec{r} - \vec{r}'|} \tag{7}$$

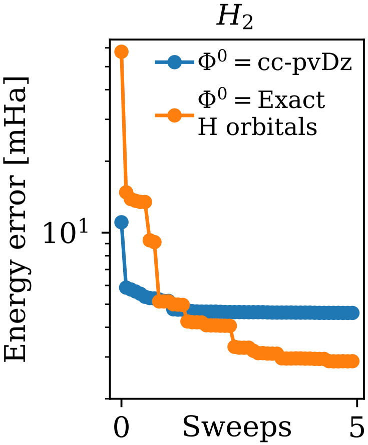
Then, we can compute the **gradients** with respect to individual orbitals :

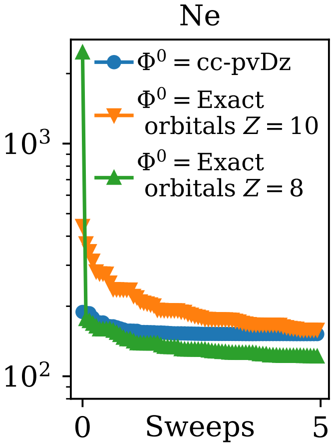
$$\xi_i(\vec{r}) = \frac{\delta E}{\delta \phi_i} = -2 \sum_j \gamma_{ij} \left[\Delta_{\vec{r}} + \frac{Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} \right] \phi_j(\vec{r}) + 2 \sum_{jk\ell} \left[\gamma_{ijk\ell} \int d\vec{r}' \frac{\phi_k \phi_\ell(\vec{r}')}{|\vec{r} - \vec{r}'|} \right] \phi_j(\vec{r}) \tag{8}$$

These gradients are in the space of orbitals, and can be used as such !

Enriching with gradients

We optimize the basis set by **feeding the gradients as orbitals** in the enrichment scheme :





Outlines

- Tensorized orbitals **extend the set of usable functions** for computational chemistry

- With tensorized orbitals, we can obtain **basis sets of arbitrary size** with **increased accuracy**, making extrapolations easier

- We can use existing basis sets or variations on exact solutions to **enrich tensorized basis sets**

- Using **gradients of the energy with respect to orbitals** improves basis sets in an agnostic manner

Thanks a lot for your attention.
Now it's time for any questions you might have !