Global Natural Orbital Functional

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Motivation

The need to overcome the drawbacks of currently used DFAs

- efficient description of strongly interacting electrons (molecular dissociation, Mott insulators, etc)

Goal

Achieve a more precise formalism than approximate density functionals, but less computationally demanding than ab initio wfn-based methods

General considerations:

- N-e$^-$ system at 0 temperature
- Time-independent functional theory for the ground state (GS)
- Non-relativistic spin-free N-electron Hamiltonian:

$$\hat{H} = \sum_{ik} \mathcal{H}_{ki} \hat{a}_k^\dagger \hat{a}_i + \frac{1}{2} \sum_{ijkl} \langle kl|ij\rangle \, \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i$$

$\mathcal{H}_{ki}$: matrix elements of kinetic energy and external potential

$\langle kl|ij\rangle$: two-particle interaction matrix elements (Coulomb integrals)

$\hat{a}_i^\dagger$ ($\hat{a}_i$): fermion creation (annihilation) operators associated with the complete orthonormal spin-orbital set $\{|i\rangle\}$.

$$\left[\hat{H}, \hat{S}^2\right] = 0, \; \left[\hat{H}, \hat{S}_z\right] = 0 \quad \Rightarrow \quad S \neq 0\text{: the GS is a Multiplet}$$

The N-electron system in a mixed state (ensemble) is described by the N-particle density matrix statistical operator:

$$\hat{\mathfrak{D}} = \sum_I \omega_I \left|\Psi_I\right\rangle \left\langle\Psi_I\right| \qquad \sum_I \omega_I = 1,\ \omega_I \geq 0$$

$$\mathfrak{D}\left(\mathbf{x}_1',\mathbf{x}_2',..,\mathbf{x}_\mathbf{N}';\mathbf{x}_1,\mathbf{x}_2,..,\mathbf{x}_\mathrm{N}\right) = \sum_I \omega_I \Psi_I\left(\mathbf{x}_1',\mathbf{x}_2',..,\mathbf{x}_\mathbf{N}'\right)\Psi_I^*\left(\mathbf{x}_1,\mathbf{x}_2,..,\mathbf{x}_\mathrm{N}\right)$$

$\Rightarrow$ ***The energy is an explicitly functional of the 1- and 2-RDMs:***

$$E\left[\mathrm{N},\Gamma,\mathrm{D}\right] = \sum_{ik} \mathcal{H}_{ik}\Gamma_{ki} + \sum_{ijkl} \left\langle ij|kl\right\rangle \mathrm{D}_{kl,ij}$$

$$\Gamma_{ki} = \sum_I \omega_I \left\langle\Psi_I\right| \hat{a}_k^\dagger \hat{a}_i \left|\Psi_I\right\rangle, \quad \mathrm{D}_{kl,ij} = \frac{1}{2}\sum_I \omega_I \left\langle\Psi_I\right| \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i \left|\Psi_I\right\rangle$$

RDM's general properties: Hermiticity, Nonnegative diagonal elements, ...

Attempts to determine the energy by minimizing $E[D]$ are complicated due to the lack of a simple set of necessary and sufficient conditions for ensuring that the two-matrix corresponds to an N-particle density matrix (N-representability).

Universal 1-RDM Fuctional:

$$E\left[\mathrm{N},\Gamma,\mathrm{D}\right] \rightarrow E\left[\mathrm{N},\Gamma\right] = \sum_{ik} \mathcal{H}_{ik}\Gamma_{ki} + V_{ee}\left[\mathrm{N},\Gamma\right]$$

$$V_{ee}\left[\mathrm{N},\Gamma\right] = \min_{E^2 \ni \mathrm{D} \rightarrow \Gamma} \left[\sum_{ijkl} \langle ij|kl\rangle \, \mathrm{D}_{kl,ij} \right] \quad \text{(Gilbert 75, Levy 79, Valone 80)}$$

$$E_{gs} = \min_{\Gamma \in E^1} \left[\mathcal{H}\left[\mathrm{N},\Gamma\right] + V_{ee}\left[\mathrm{N},\Gamma\right] \right]$$

1. limiting situations $\rightarrow$ minimization can be exactly solved
   In general, const. search is not appropriate for computation
2. $V_{ee}\left[\mathrm{N},\Gamma\right]$ has been unreachable so far $\Rightarrow$ We have to settle for approximations

Spectral decomposition of the 1RDM: $\Gamma(\mathbf{x}_1', \mathbf{x}_1) = \sum_i n_i \phi_i(\mathbf{x}_1') \phi_i^*(\mathbf{x}_1)$

$\{\phi_i(\mathbf{x})\}$: **natural spin-orbitals** $\{n_i\}$: **occupation numbers**

- The 1RDM in the natural orbital (NO) representation: $\Gamma_{ki} = n_i \delta_{ki}$
- Ensemble N-representable 1RDM:

$$0 \leq n_i \leq 1, \ \sum_i n_i = \mathrm{N} \quad \text{(Coleman 1963)}$$

- The **universal functional in NO representation**:

$$E_{gs} = \min_{\{n_i, \phi_i\} \in E^1} \left\{ \sum_i n_i \mathcal{H}_{ii} + V_{ee}[\mathrm{N}, \{n_i, \phi_i\}] \right\}$$

$$V_{ee}[\mathrm{N}, \{n_i, \phi_i\}] = \min_{E^2 \ni \mathrm{D} \to \{n_i, \phi_i\}} \left\{ \sum_{ijkl} \langle ij|kl \rangle \mathrm{D}_{kl,ij} \right\}$$

Approximate 2RDM $D[n_i, n_j, n_k, n_l]$:

$$E \approx \sum_i n_i \mathcal{H}_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l] \langle ij|kl\rangle, \qquad E_{gs} = \min_{\{n_i,\phi_i\}\in E^{\mathbf{1}}} E\left[\mathrm{N}, \{n_i, \phi_i\}\right]$$

- V_{ee} will not, in general, be entirely rebuilt
  An approximate NOF still depends on D (Donnelly 79)

- The N-representability is twofold:

N-representable 1RDM	N-representable Functional
$\mathfrak{D} \to \Gamma : 0 \leq n_i \leq 1,\ \sum_i n_i = \mathrm{N}$	$\mathfrak{D} \to \mathrm{D} : E\left[\mathfrak{D}\right] \to E\left[\mathrm{N}, \{n_i, \phi_i\}\right]$

  For the 2RDM, a complete set of N-representability conditions that do not depend on higher-order RDMs remains unknown.

- Alternative: Use the (2,2)-positivity conditions $\mathbf{D} \geq 0$, $\mathbf{Q} \geq 0$, $\mathbf{G} \geq 0$

Singlet State in a two-electron system

- Exact Wavefunction & Energy (Lowdin & Shull 1955)

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \alpha_2\beta_1)\sum_p f_p\sqrt{n_p}\varphi_p(\mathbf{r}_1)\varphi_p(\mathbf{r}_2), \quad f_p = \pm 1$$

$$E[\mathrm{N}, \{f_p, n_p, \varphi_p\}] = 2\sum_p n_p H_{pp} + \sum_{p,q} f_p f_q \sqrt{n_q n_p} L_{pq}, \quad L_{pq} = \langle pp|qq\rangle$$

Phase Dilemma: # of possible $\{f_p\}$ combinations is prohibitively large

- NOF: $E(2e^-) = 2\sum_p n_p H_{pp} + n_1 L_{11} - 2\sum_{p=2}\sqrt{n_1 n_p} L_{p1} + \sum_{p,q=2}\sqrt{n_q n_p} L_{pq}$

Accurate NOF $\Rightarrow$ Motivation for using **electron-pairs as basic units!**

- Electron-pairing-based NOFs for N electrons: $D^{\alpha\alpha}_{pq,rt}, D^{\beta\beta}_{pq,rt}, D^{\alpha\beta}_{pq,rt}$

- PNOF5, PNOF6, PNOF7 [Phys. Rev. Lett. 119, 063002, 2017] (static)

- GNOF [Phys. Rev. Lett. 127, 233001, 2021] (static + dynamic correlation)

The adjective 'global' is used instead of 'universal': GNOF $\neq$ Valone's exact.

GNOF for Singlet States: $E = E^{intra} + E^{inter}$

1. $$E^{intra} = \sum_{g=1}^{N/2} E_g, \quad E_g = \sum_{p\in\Omega_g} n_p \left(2H_{pp} + L_{pp}\right) + \sum_{q,p\in\Omega_g, p\neq q} \Pi\left(n_q, n_p\right) L_{pq}$$

$$\Pi\left(n_q, n_p\right) = \sqrt{n_q n_p}\left(\delta_{q\Omega^a}\delta_{p\Omega^a} - \delta_{qg} - \delta_{pg}\right)$$

2. $$E^{inter} = \sum_{p,q=1}^{N_B}{}' \left\{ n_q n_p \left(2J_{pq} - K_{pq}\right) + \left(1 - \delta_{q\Omega^b}\delta_{p\Omega^b}\right) \left[n_q^d n_p^d + \Pi\left(n_q^d, n_p^d\right) - \sqrt{n_q h_q n_p h_p}\right] L_{pq} \right\}$$

$$n_p^d = n_p \cdot e^{-\left(\frac{h_g}{h_c}\right)^2}, \quad h_c = 0.02\sqrt{2}\,, \quad p \in \Omega_g\,, \quad g = \overline{1, N/2}$$

GNOF for Spin Multiplets:

$$<\hat{S}_z> = \sum_{M=-S}^{S} \omega_M \langle SM|\,\hat{S}_z\,|SM\rangle = 0 \quad \Rightarrow$$ the spin-restricted theory can be adopted

Total Spin: $<\hat{S}^2> = \frac{N_I}{2}\left(\frac{N_I}{2} + 1\right) \quad \rightarrow \quad S = \frac{N_I}{2}, \quad 2S + 1 = N_I + 1$

Total energies (Hartrees)

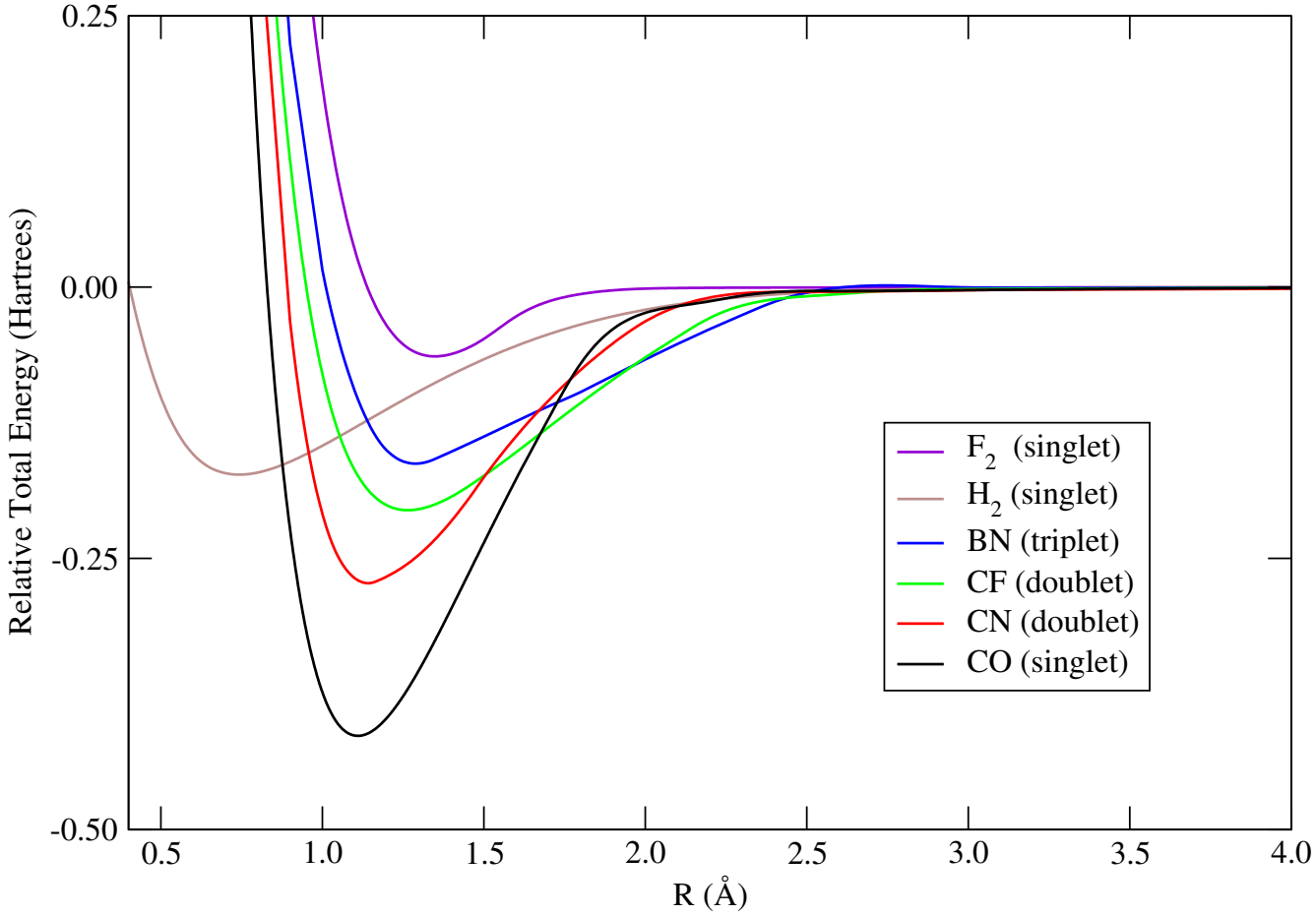
Atoms (aug-cc-pVTZ)

At	GS	GNOF	CCSD(T)
H	^2S	-0.49983	-0.49983
He	^1S	-2.90084	-2.90084
Li	^2S	-7.45318	-7.45338
Be	^1S	-14.63382	-14.63565
B	^2P	-24.60751	-24.60912
C	^3P	-37.79635	-37.79712
N	^4S	-54.52947	-54.53421
O	^3P	-75.00049	-74.99967
F	^2P	-99.65391	-99.65218
Ne	^1S	-128.8442	-128.8440
MAE (10)		0.0012	-

Molecules at the Exp. Geom. (cc-pVTZ)

Molecule	MP2	GNOF	CCSD(T)
CH_4	-40.43238	-40.45533	-40.45960
C_2H_6	-79.67171	-79.71166	-79.71789
H_2CO	-114.34175	-114.36809	-114.36928
HCOOH	-189.51455	-189.54192	-189.54659
C_2FH_3	-177.58430	-177.62610	-177.62758
C_2H_5N	-133.70022	-133.73644	-133.74992
$C_2H_2O_2$	-227.51149	-227.54481	-227.55734
CH_3NH_2	-95.69653	-95.73376	-95.73676
CH_3OCH_3	-154.78170	-154.83262	-154.83576
CH_3CH_2OH	-154.80194	-154.84906	-154.85458
...	...	...	...
MAE (55)	30 mHa	8 mHa	-

Potential Energy Curves

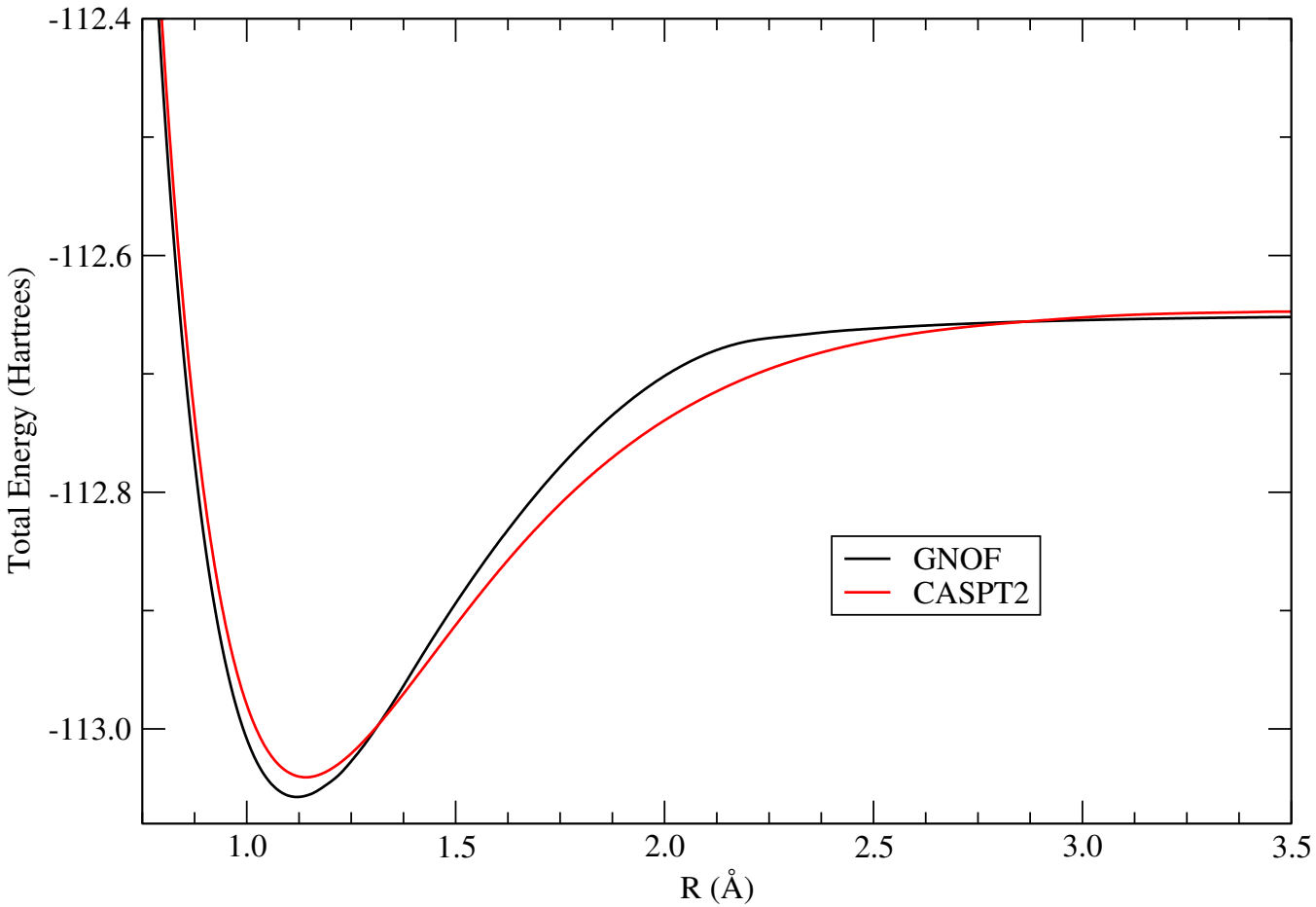


Comparison with the Experimental Data

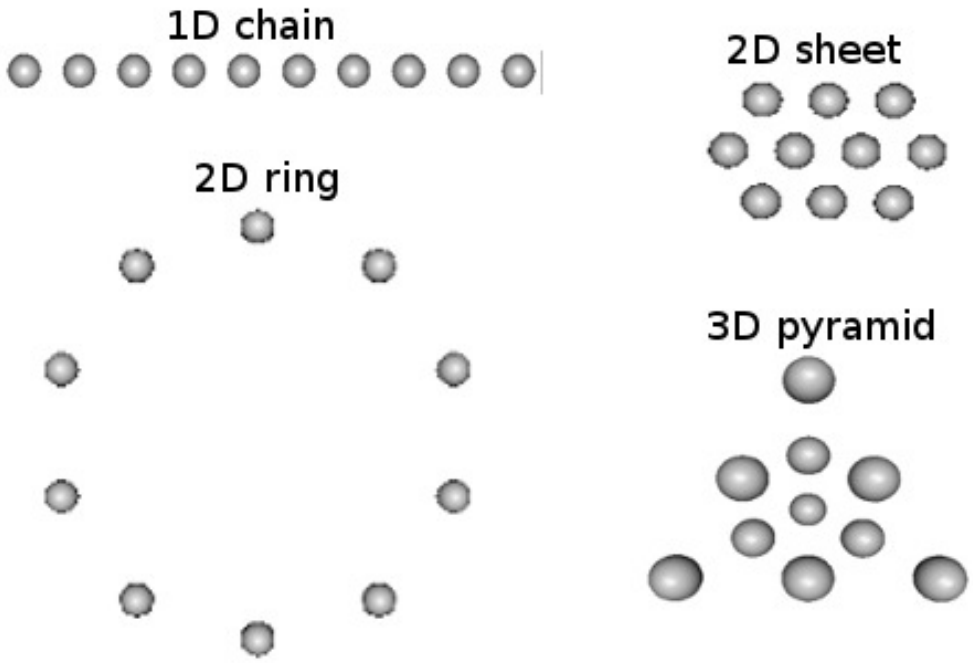
Mol	Mul	R_e	R_e^{exp}	D_e	D_e^{exp}	ω_e	ω_e^{exp}
F_2	1	1.35	1.41	40.9	39.2	1212	917
H_2	1	0.74	0.74	108.6	109.5	4404	4401
BN	3	1.29	1.32	102.3	94-133	1851	1515
CN	2	1.14	1.17	171.6	177.4	2344	2069
CF	2	1.26	1.27	129.0	128.7	1238	1308
CO	1	1.11	1.13	259.6	259.3	2391	2170

R_e (Å), D_e (kcal/mol), and ω_e (cm^{-1})

PECs for the singlet ground state of the CO

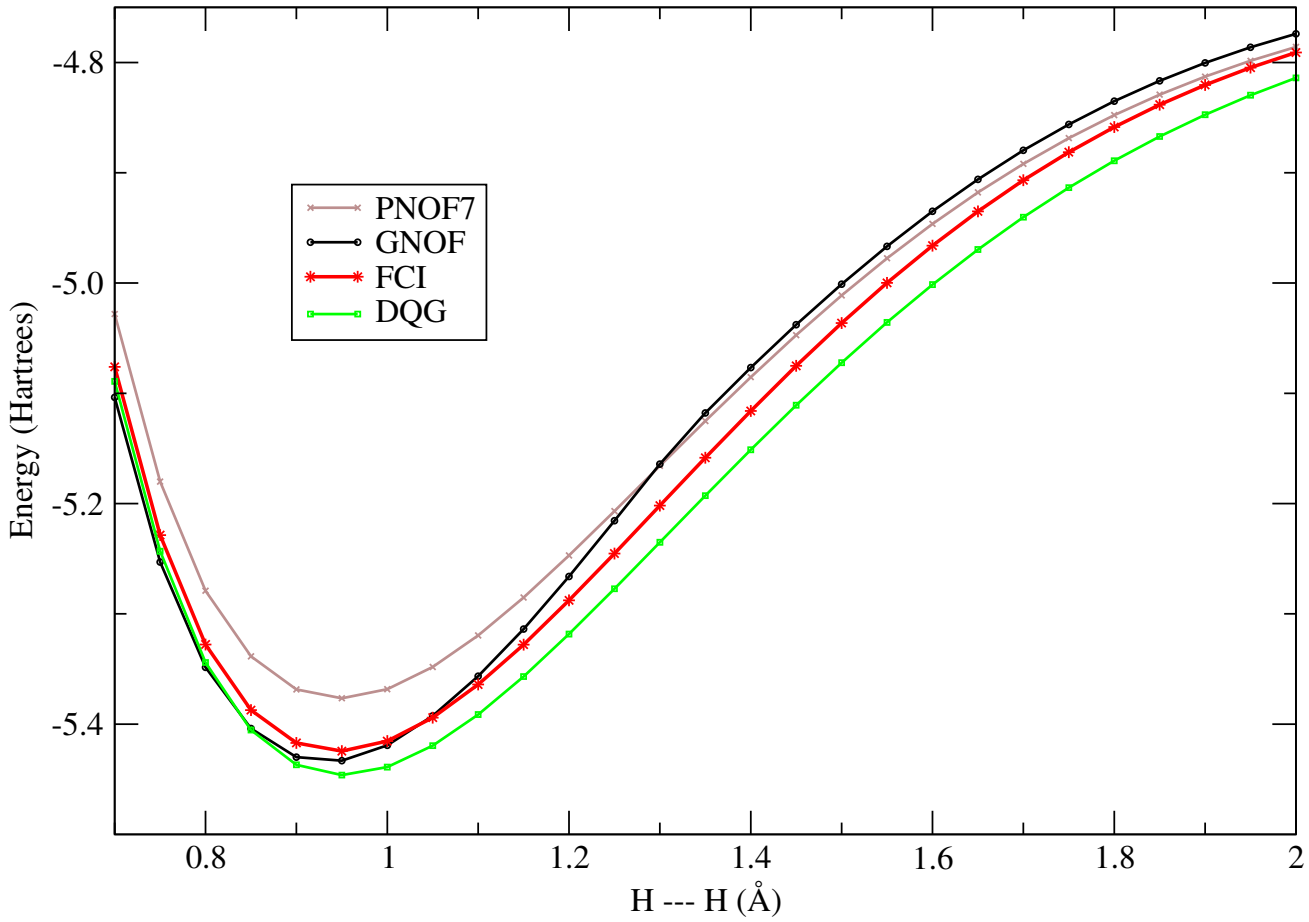


Benchmarking GNOF against FCI in one, two and three dimensions

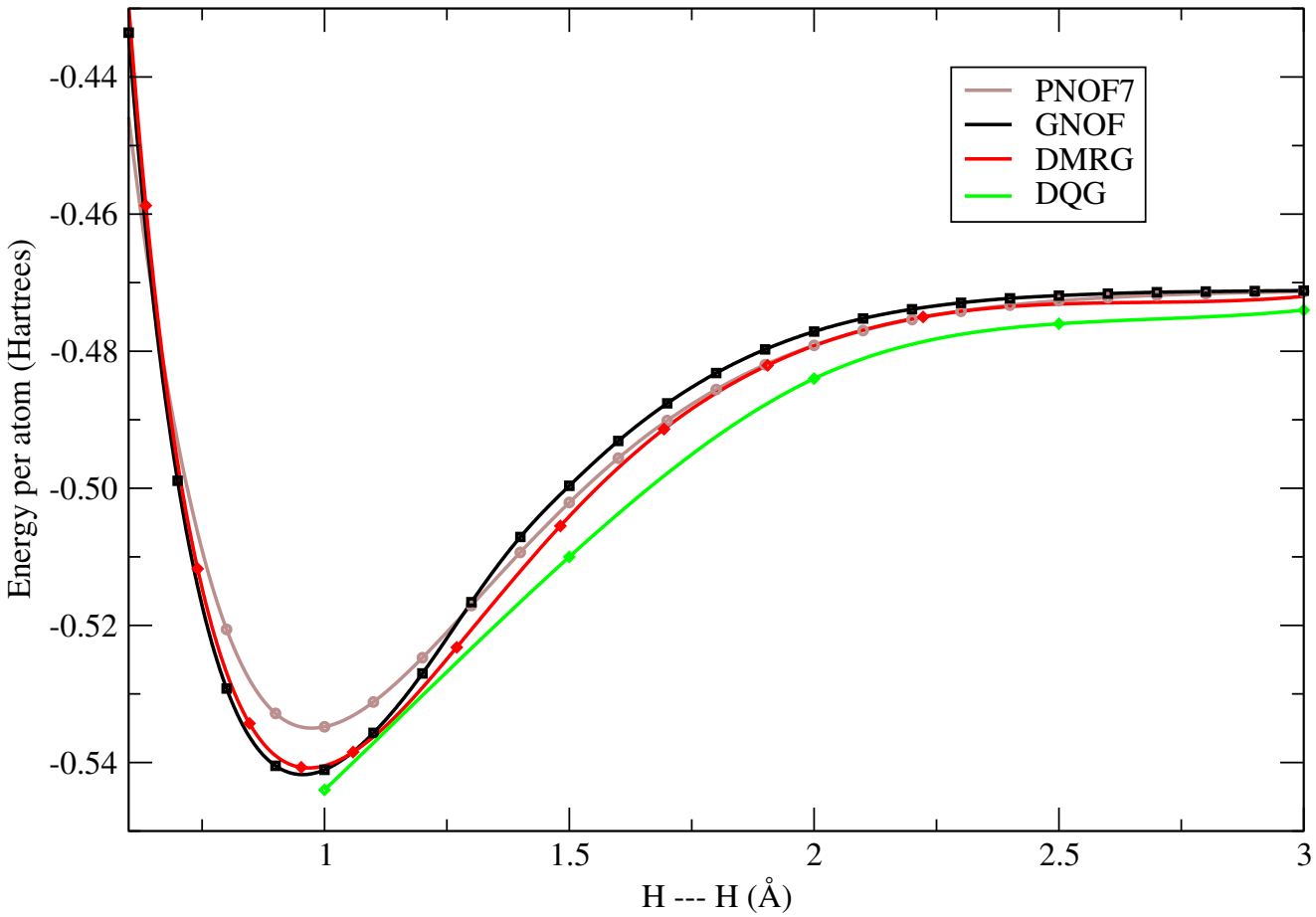


I. Mitxelena & M. Piris, J. Chem. Phys. 156, 214102 (2022)

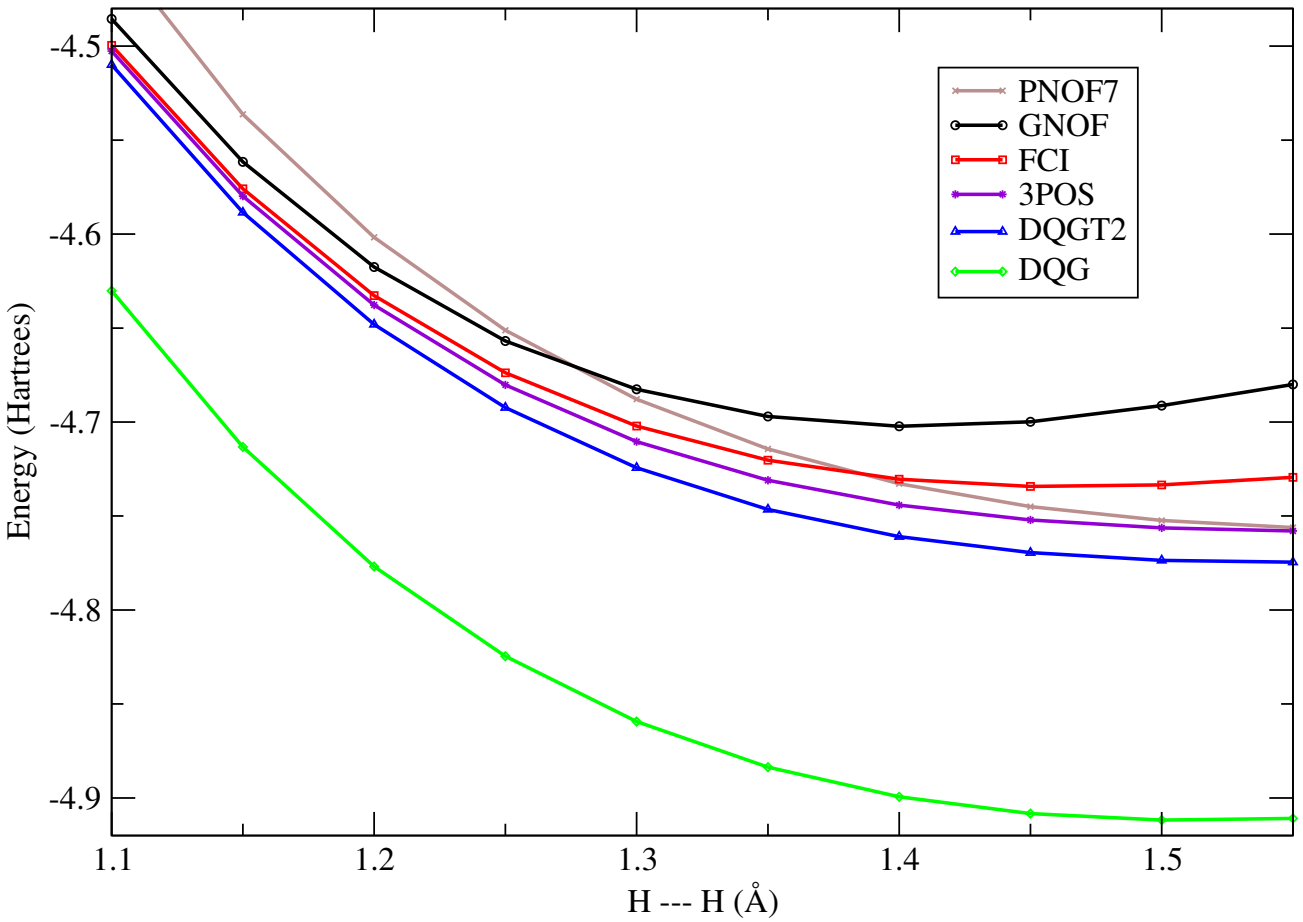
Dissociation curves corresponding to a **1D lineal chain** of 10 H



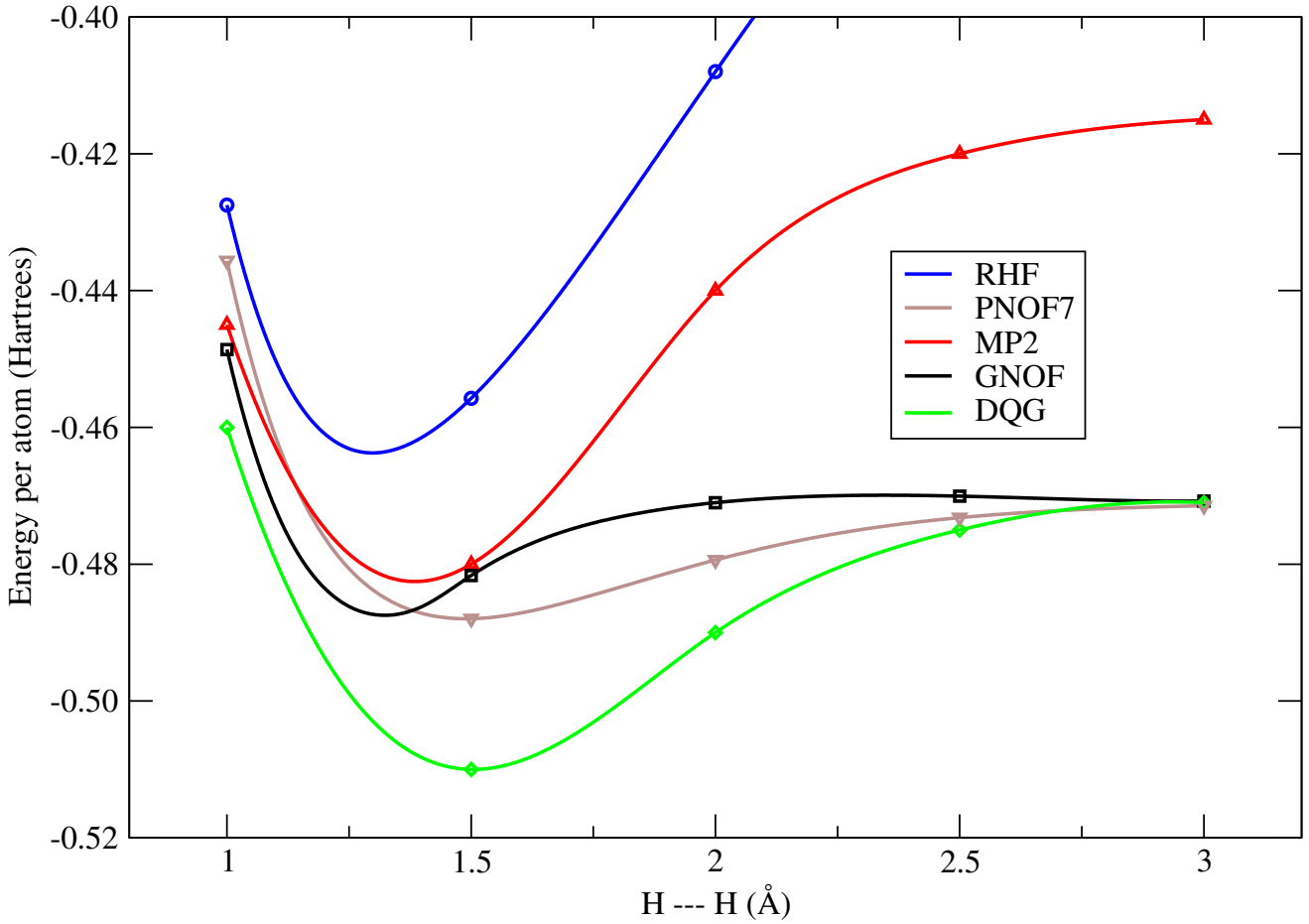
Dissociation curves corresponding to a **1D lineal chain** of 50 H



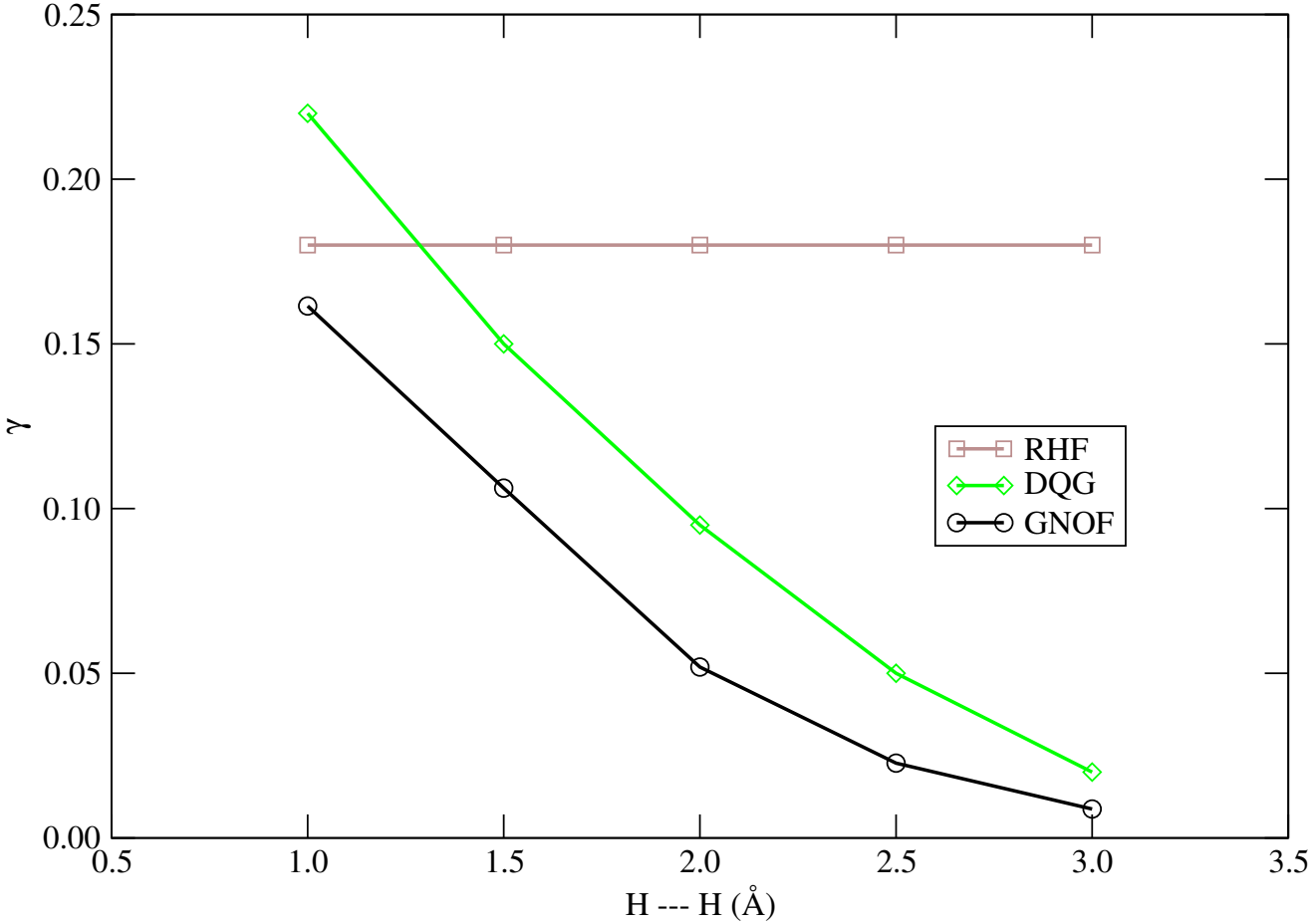
Dissociation curves corresponding to a **3D pyramid** of 10 H



Symmetric dissociation energy curves corresponding to a **4 × 4 × 4 hydrogen cube**.

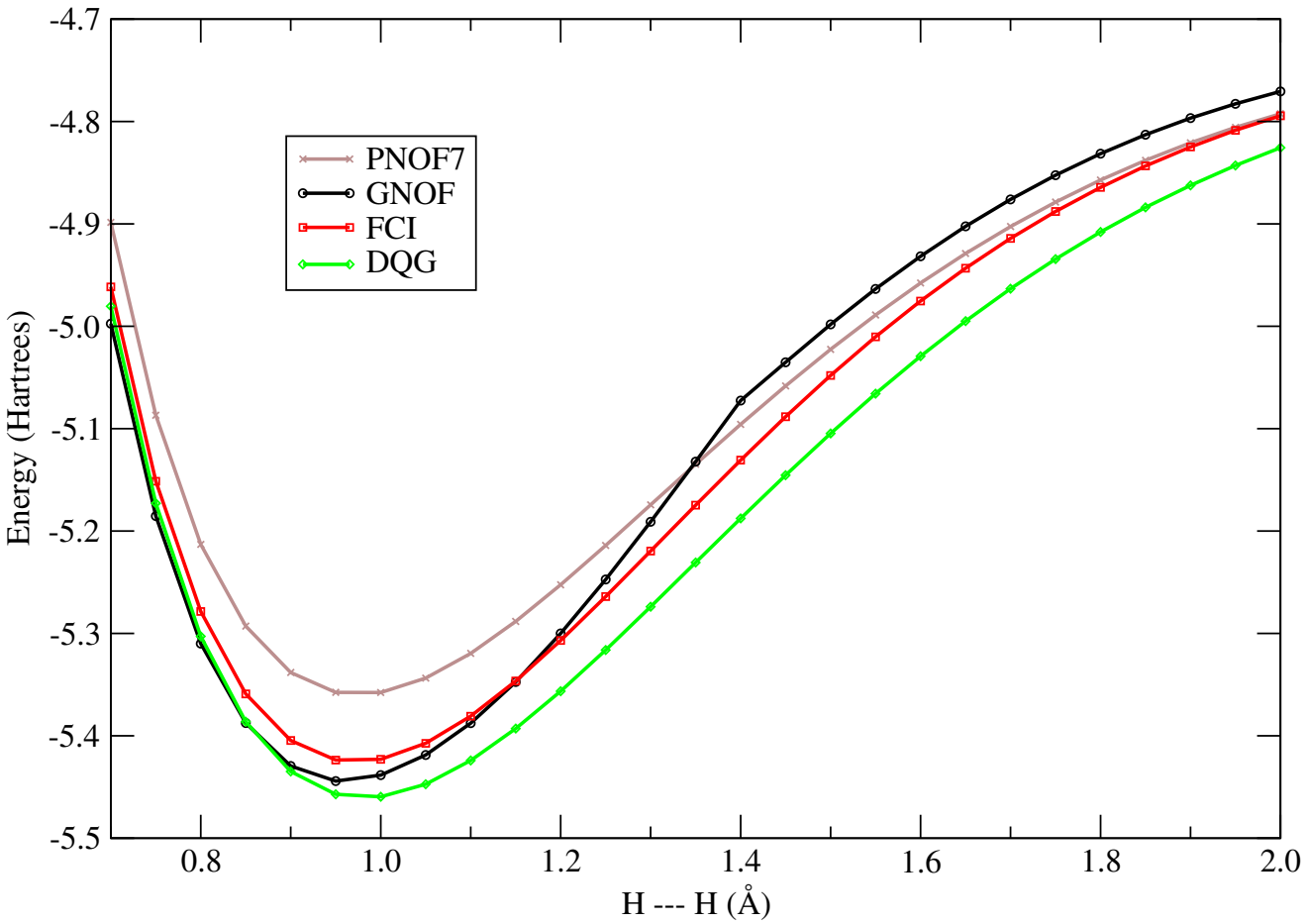


Metal-to-insulator transition in the $4 \times 4 \times 4$ **hydrogen cube**

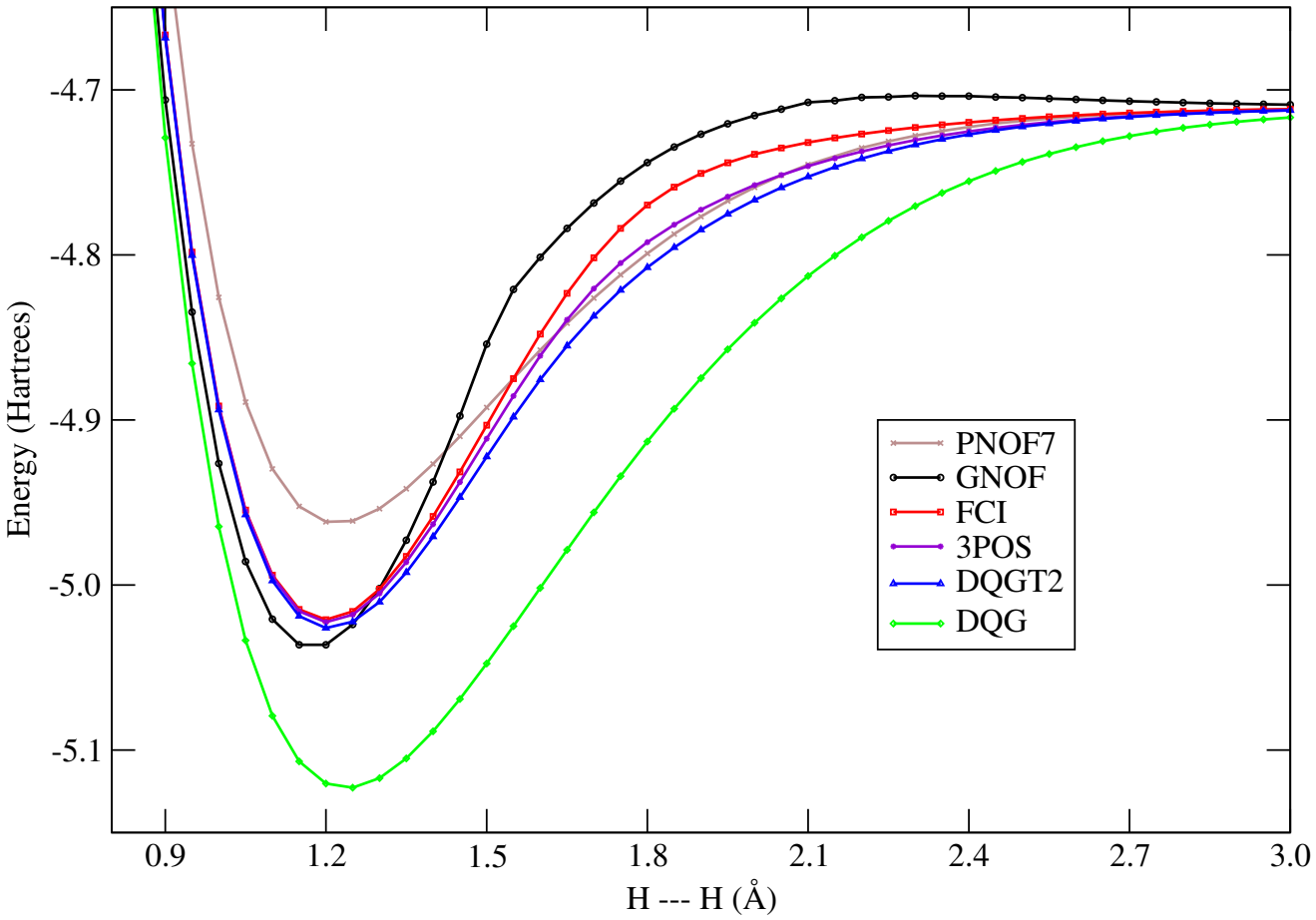


Average of off-diagonal 1RDM elements: $\gamma = \sqrt{\frac{1}{N(N-1)} \sum_{i \neq j} (\Gamma_{ij}^{AO})^2}$

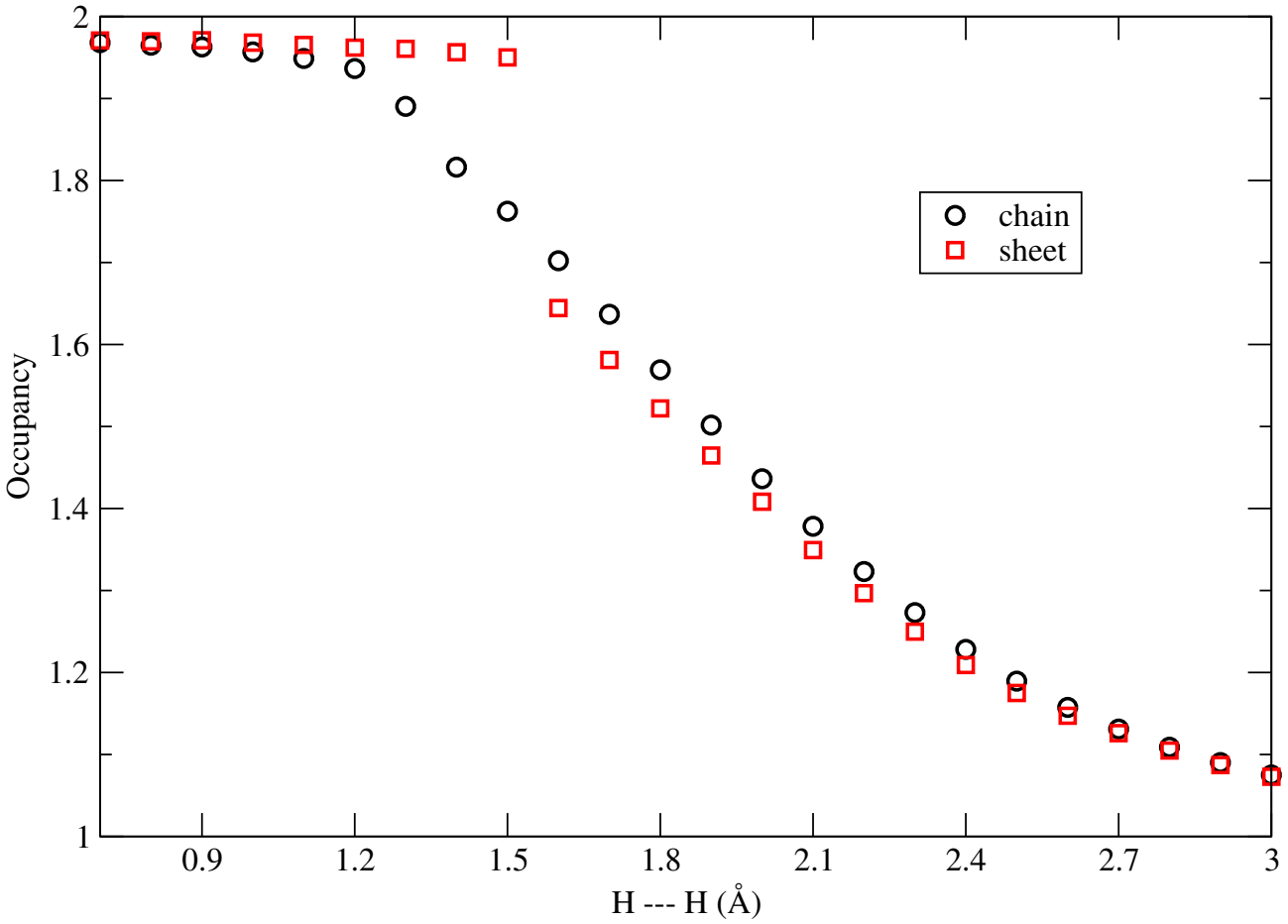
Dissociation curves corresponding to a **2D ring** of 10 H



Dissociation curves corresponding to a **2D sheet** of 10 H



Occupancy ($2n_p$) of the lowest strongly occupied natural orbital



Donostia Natural Orbital Functional Program

https://github.com/DoNOF/DoNOFsw

- Unconstrained Occupancy Optimization
- Self-consistent iterative diagonalization procedure for NOs
- Geometry optimization (analytic gradients)
- Harmonic vibrational frequencies (numerical Hessian)
- Natural and canonical representations of molecular orbitals
- Ionization potential using extended Koopmans' Theorem (EKT)

More details in https://donof.readthedocs.io/

Closing remarks

- Approximate NOF still depends on the 2RDM:

  Functional N-representability

- GNOF: recover dynamic and non-dynamic correlations

Thank you for your attention !!!