

# 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<sup>-</sup> 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  $\{|i\rangle\}$ .

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

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

$$\hat{\mathcal{D}} = \sum_I \omega_I |\Psi_I\rangle \langle \Psi_I| \quad \sum_I \omega_I = 1, \omega_I \geq 0$$

$$\mathcal{D}(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N; \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum_I \omega_I \Psi_I(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N) \Psi_I^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

⇒ *The energy is an explicitly functional of the 1- and 2-RDMs:*

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

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

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

## Universal 1-RDM Functional:

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

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

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

- 1 limiting situations  $\rightarrow$  minimization can be exactly solved  
In general, const. search is not appropriate for computation
- 2  $V_{ee} [N, \Gamma]$  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:

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

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

$$E_{gs} = \min_{\{n_i, \phi_i\} \in \mathcal{E}^1} \left\{ \sum_i n_i \mathcal{H}_{ii} + V_{ee} [N, \{n_i, \phi_i\}] \right\}$$
$$V_{ee} [N, \{n_i, \phi_i\}] = \min_{\mathcal{E}^2 \ni \mathcal{D} \rightarrow \{n_i, \phi_i\}} \left\{ \sum_{ijkl} \langle ij | kl \rangle D_{kl, ij} \right\}$$

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

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

- $V_{ee}$  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

$$\mathcal{D} \rightarrow \Gamma : 0 \leq n_i \leq 1, \sum_i n_i = N$$

$$\mathcal{D} \rightarrow D : E[\mathcal{D}] \rightarrow E[N, \{n_i, \phi_i\}]$$

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)

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

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

**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!**

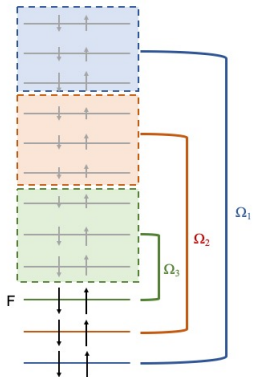
- Electron-pairing-based NOFs for N electrons:  $D_{pq,rt}^{\alpha\alpha}, D_{pq,rt}^{\beta\beta}, D_{pq,rt}^{\alpha\beta}$ 
  - PNOF5, PNOF6, PNOF7 [Phys. Rev. Lett. 119, 063002, 2017] (static)
  - GNOF [Phys. Rev. Lett. 127, 233001, 2021] (static + dynamic correlation)

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



# Singlet

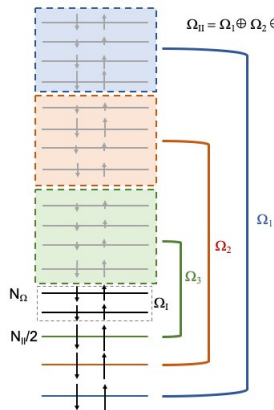
Orbital Space  $\Omega = \Omega_1 \oplus \Omega_2 \oplus \Omega_3$



# Triplet

$\Omega = \Omega_1 \oplus \Omega_{11}$

$\Omega_{11} = \Omega_1 \oplus \Omega_2 \oplus \Omega_3$



## GNOF for Singlet States

$$E = E^{intra} + E^{inter}$$

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

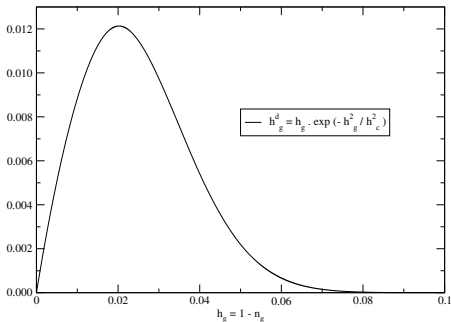
$$\Pi(n_q, n_p) = \sqrt{n_q n_p} (\delta_{q\Omega^a} \delta_{p\Omega^a} - \delta_{qg} - \delta_{pg})$$

$$\textcircled{2} \quad E^{inter} = \sum_{p, q=1}^{N^B} ' \left\{ \begin{aligned} & n_q n_p (2J_{pq} - K_{pq}) + (1 - \delta_{q\Omega^b} \delta_{p\Omega^b}) \\ & [n_q^d n_p^d + \Pi(n_q^d, n_p^d) - \sqrt{n_q h_q n_p h_p}] L_{pq} \end{aligned} \right\}$$

- prime indicates that only the inter-subspace terms are taking into account ( $p \in \Omega_f, q \in \Omega_g, f \neq g$ ).

## Dynamic Hole and Occupation Number

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



Dynamic hole for  $h_c = 0.02\sqrt{2}$ .

## GNOF for Multilet States: $N = N_{II} + N_I$

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

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

$$E = E_{\text{intra}} + E_{\text{HF}}^{\text{inter}} + E_{\text{sta}}^{\text{inter}} + E_{\text{dyn}}^{\text{inter}}, \quad N_{\Omega} = N_{II}/2 + N_I$$

$$E_{\text{intra}} = \sum_{g=1}^{N_{II}/2} E_g + \sum_{g=N_{II}/2+1}^{N_{\Omega}} H_{gg}, \quad E_{\text{HF}}^{\text{inter}} = \sum_{p,q=1}^{N_B} ' n_q n_p (2J_{pq} - K_{pq})$$

$$E_{\text{sta}}^{\text{inter}} = - \left( \sum_{p=1}^{N_{\Omega}} \sum_{q=N_{\Omega}+1}^{N_B} + \sum_{p=N_{\Omega}+1}^{N_B} \sum_{q=1}^{N_{\Omega}} + \sum_{p,q=N_{\Omega}+1}^{N_B} \right) ' \sqrt{n_q h_q n_p h_p} L_{pq}$$

$$- \frac{1}{2} \left( \sum_{p=1}^{N_{II}/2} \sum_{q=N_{II}/2+1}^{N_{\Omega}} + \sum_{p=N_{II}/2+1}^{N_{\Omega}} \sum_{q=1}^{N_{II}/2} \right) ' \sqrt{n_q h_q n_p h_p} L_{pq} - \frac{1}{4} \sum_{p,q=N_{II}/2+1}^{N_{\Omega}} K_{pq}$$

$$E_{\text{dyn}}^{\text{inter}} = - \left( \sum_{p=1}^{N_{II}/2} \sum_{q=N_{\Omega}+1}^{N_B} + \sum_{p=N_{\Omega}+1}^{N_B} \sum_{q=1}^{N_{II}/2} \right) ' \left( \sqrt{n_q^d n_p^d} - n_q^d n_p^d \right) L_{pq}$$

$$+ \sum_{p,q=N_{\Omega}+1}^{N_B} ' \left( \sqrt{n_q^d n_p^d} + n_q^d n_p^d \right) L_{pq}$$

## Total energies (Hartrees)

### Atoms (aug-cc-pVTZ)

Atom	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

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

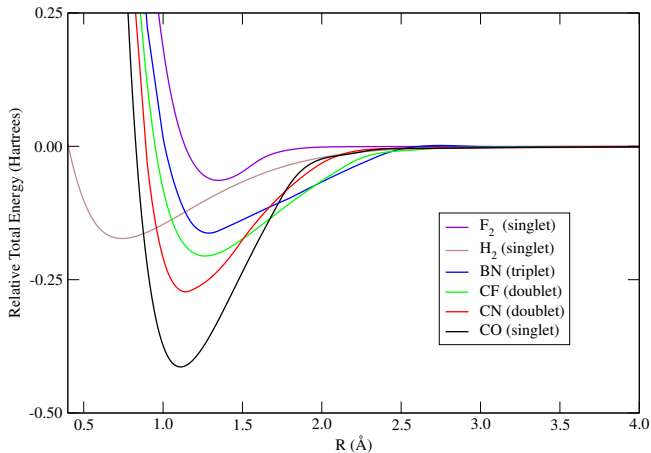
Molecule	MP2	GNOF	CCSD(T)
CH <sub>4</sub>	-40.43238	-40.45533	-40.45960
C <sub>2</sub> H <sub>6</sub>	-79.67171	-79.71166	-79.71789
H <sub>2</sub> CO	-114.34175	-114.36809	-114.36928
HCOOH	-189.51455	-189.54192	-189.54659
C <sub>2</sub> FH <sub>3</sub>	-177.58430	-177.62610	-177.62758
C <sub>2</sub> H <sub>5</sub> N	-133.70022	-133.73644	-133.74992
C <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	-227.51149	-227.54481	-227.55734
CH <sub>3</sub> NH <sub>2</sub>	-95.69653	-95.73376	-95.73676
CH <sub>3</sub> OCH <sub>3</sub>	-154.78170	-154.83262	-154.83576
CH <sub>3</sub> CH <sub>2</sub> OH	-154.80194	-154.84906	-154.85458
...	...	...	...
<b>MAE (55)</b>	<b>30 mHa</b>	<b>8 mHa</b>	-

MAE (10)

0.0012

-

# Potential Energy Curves

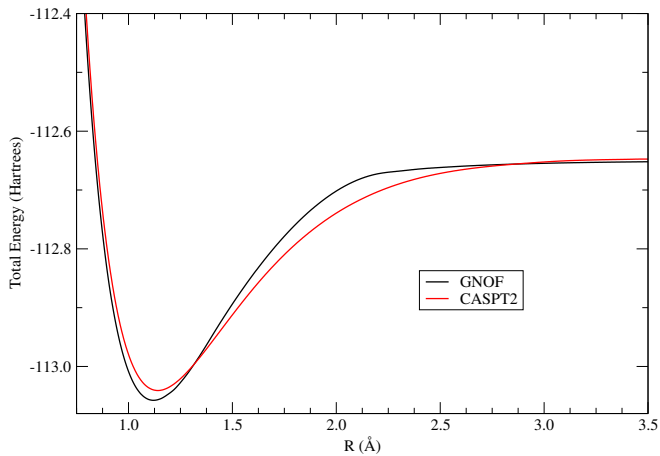


## Comparison with the Experimental Data

Mol	Mul	$R_e$	$R_e^{exp}$	$D_e$	$D_e^{exp}$	$\omega_e$	$\omega_e^{exp}$
F <sub>2</sub>	1	1.35	1.41	40.9	39.2	1212	917
H <sub>2</sub>	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

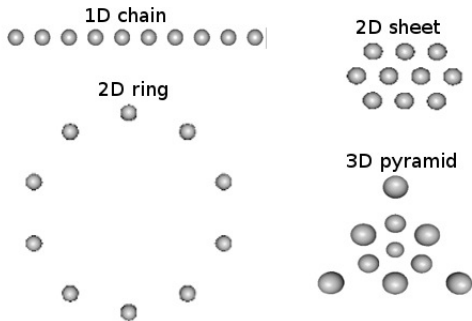
$R_e$  (Å),  $D_e$  (kcal/mol), and  $\omega_e$  (cm<sup>-1</sup>)

## PECs for the singlet ground state of the CO



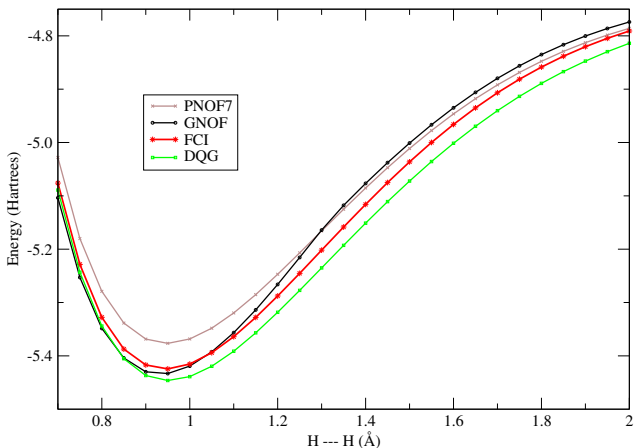


# Benchmarking GNOF against FCI in one, two and three dimensions

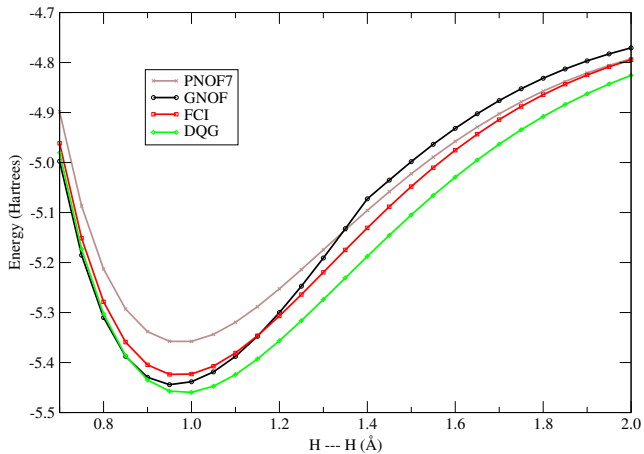


I. Mitxelena & M. Piris, J. Chem. Phys. 156, 214102 (2022)

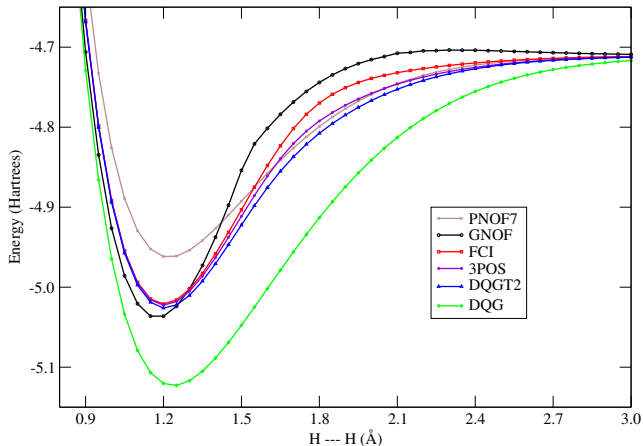
# Dissociation curves corresponding to a 1D lineal chain of 10 H



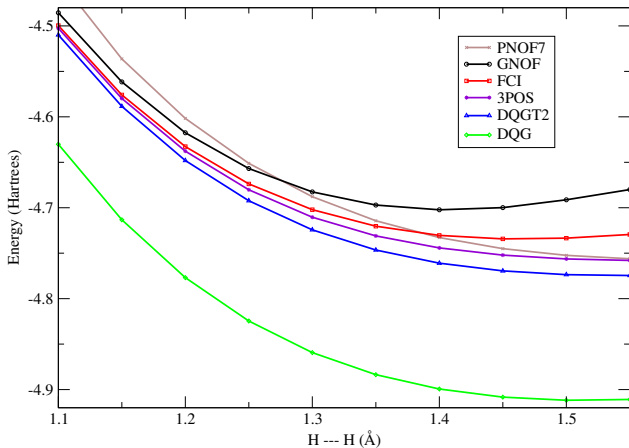
## Dissociation curves corresponding to a 2D ring of 10 H



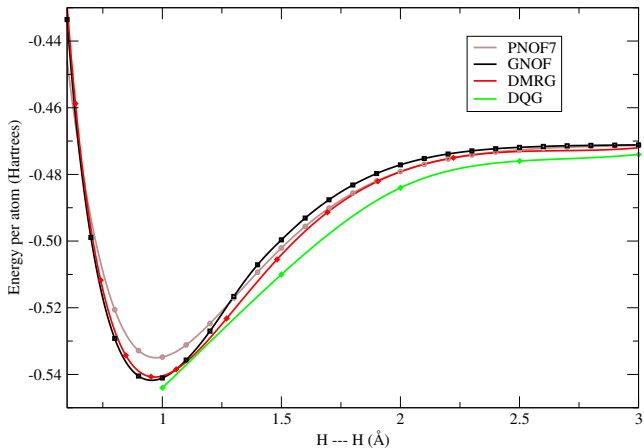
## Dissociation curves corresponding to a 2D sheet of 10 H



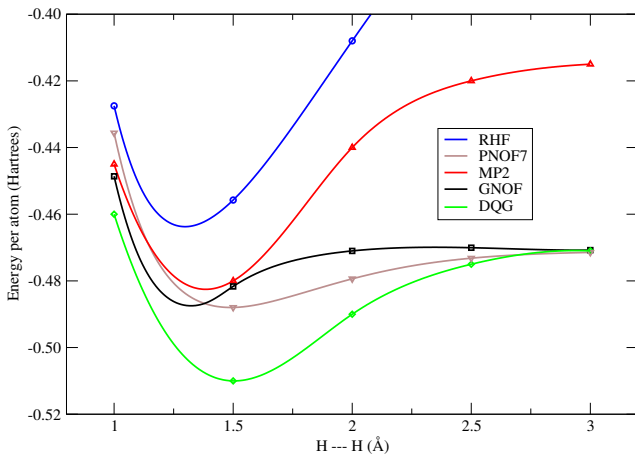
# Dissociation curves corresponding to a 3D pyramid of 10 H



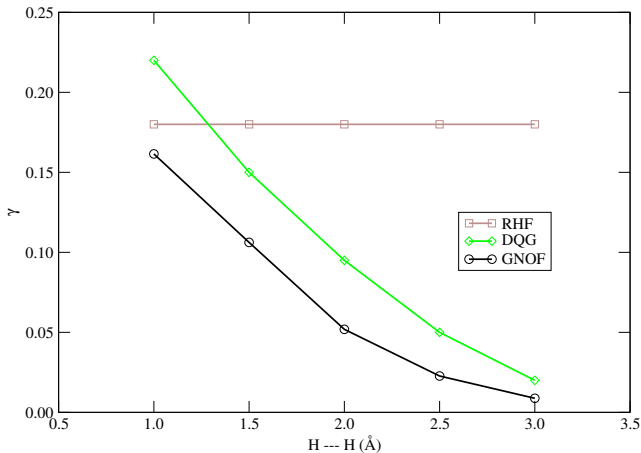
# Dissociation curves corresponding to a 1D lineal chain of 50 H



# Symmetric dissociation energy curves corresponding to a $4 \times 4 \times 4$ hydrogen cube.



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



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



# 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/>

- Approximate NOF still depends on the 2RDM:  
Functional N-representability
- GNOF: recover dynamic and non-dynamic correlations

Thank you for your attention !!!