

GNOF: Balanced treatment of electron correlation

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June 23, 2023



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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 accurate formalism than approximate density functionals, but less computationally demanding than ab initio wavefunction-based methods

Outline

- Introduction to the Natural Orbital Functional Theory (NOFT)
 - Reduced Density Matrices (RDMs)
 - N-representability
 - 2RDM reconstruction in terms of 1RDM: : $D[n_i, n_j, n_k, n_l]$
 - Electron-pairing-based NOFs → GNOF
- Born-Oppenheimer Molecular Dynamics (BO-MD) based on an accurate NOF approximation (GNOF)

General considerations

- N-electron system at 0 temperature
- The ground state (GS)
- Non-relativistic spin-free N-electron Hamiltonian:

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

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

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

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

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

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

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

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

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, constrained 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: $0 \leq n_i \leq 1, \sum_i n_i = N$
- The universal functional in NO representation:

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

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

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**

The N-representability is twofold:

1) N-representable 1RDM

2) 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 $D \geq 0, Q \geq 0, G \geq 0$

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: $E(2e^-) = 2 \sum_p n_p H_{pp} + n_1 L_{11} - 2 \sum_{p=2}^1 \sqrt{n_1 n_p} L_{p1} + \sum_{p,q=2} \sqrt{n_q n_p} L_{pq}$

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

Electron-pairing-based NOFs for N electrons:

$$D_{pq,rt}^{\alpha\alpha} ; D_{pq,rt}^{\alpha\beta} ; D_{pq,rt}^{\beta\beta}$$

I. PNOF5, PNOF6, PNOF7 [Phys. Rev. Lett. 119, 063002, 2017]

Static electron correlation

II. GNOF [Phys. Rev. Lett. 127, 233001, 2021]

Static + Dynamic electron correlation

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

GNOF for Singlet States

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

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

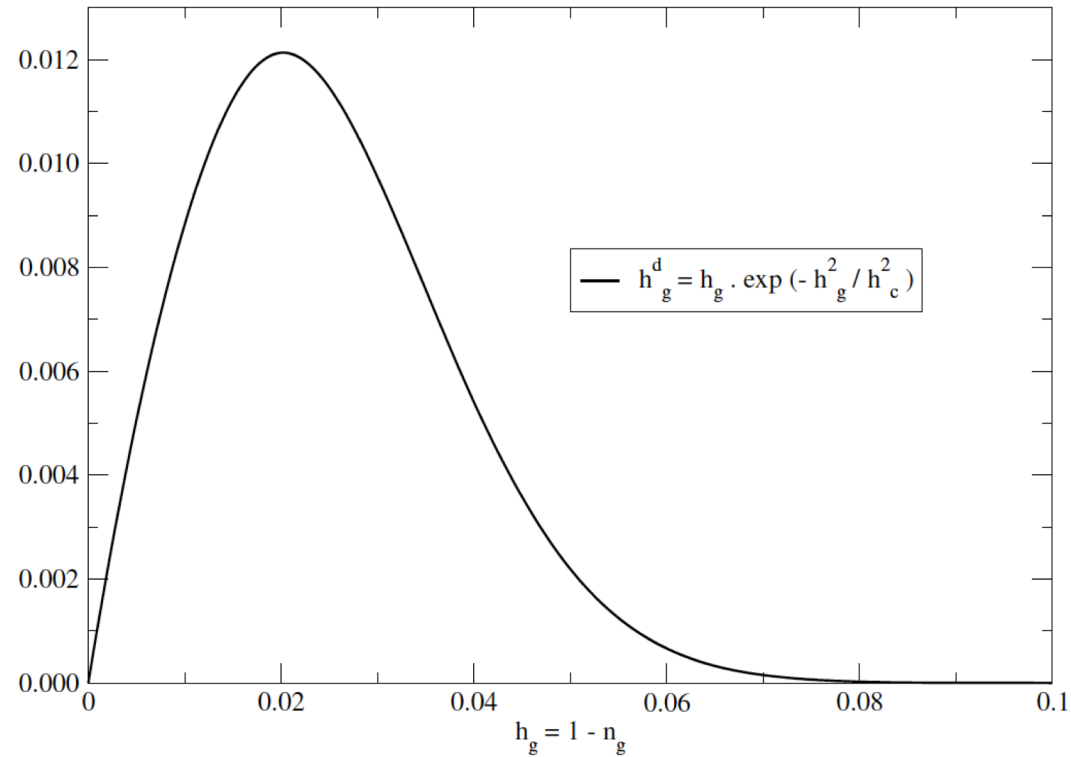
$$\Pi(n_q, n_p) = \sqrt{n_q n_p} (\delta_{q\Omega^a} \delta_{p\Omega^a} - \delta_{qg} - \delta_{pg})$$

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

- 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: $N = N_{II} + N_I$

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

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

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

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

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

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

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

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

Total energies (Hartrees)

Atoms (aug-cc-pVTZ)

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

Atom	State	GNOF	CCSD(T)	Molecule	MP2	GNOF	CCSD(T)
At	GS						
H	2S	-0.49983	-0.49983	CH ₄	-40.43238	-40.45533	-40.45960
He	1S	-2.90084	-2.90084	C ₂ H ₆	-79.67171	-79.71166	-79.71789
Li	2S	-7.45318	-7.45338	H ₂ CO	-114.34175	-114.36809	-114.36928
Be	1S	-14.63382	-14.63565	HCOOH	-189.51455	-189.54192	-189.54659
B	2P	-24.60751	-24.60912	C ₂ FH ₃	-177.58430	-177.62610	-177.62758
C	3P	-37.79635	-37.79712	C ₂ H ₅ N	-133.70022	-133.73644	-133.74992
N	4S	-54.52947	-54.53421	C ₂ H ₂ O ₂	-227.51149	-227.54481	-227.55734
O	3P	-75.00049	-74.99967	CH ₃ NH ₂	-95.69653	-95.73376	-95.73676
F	2P	-99.65391	-99.65218	CH ₃ OCH ₃	-154.78170	-154.83262	-154.83576
Ne	1S	-128.8442	-128.8440	CH ₃ CH ₂ OH	-154.80194	-154.84906	-154.85458

...

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MAE (10)

0.0012

-

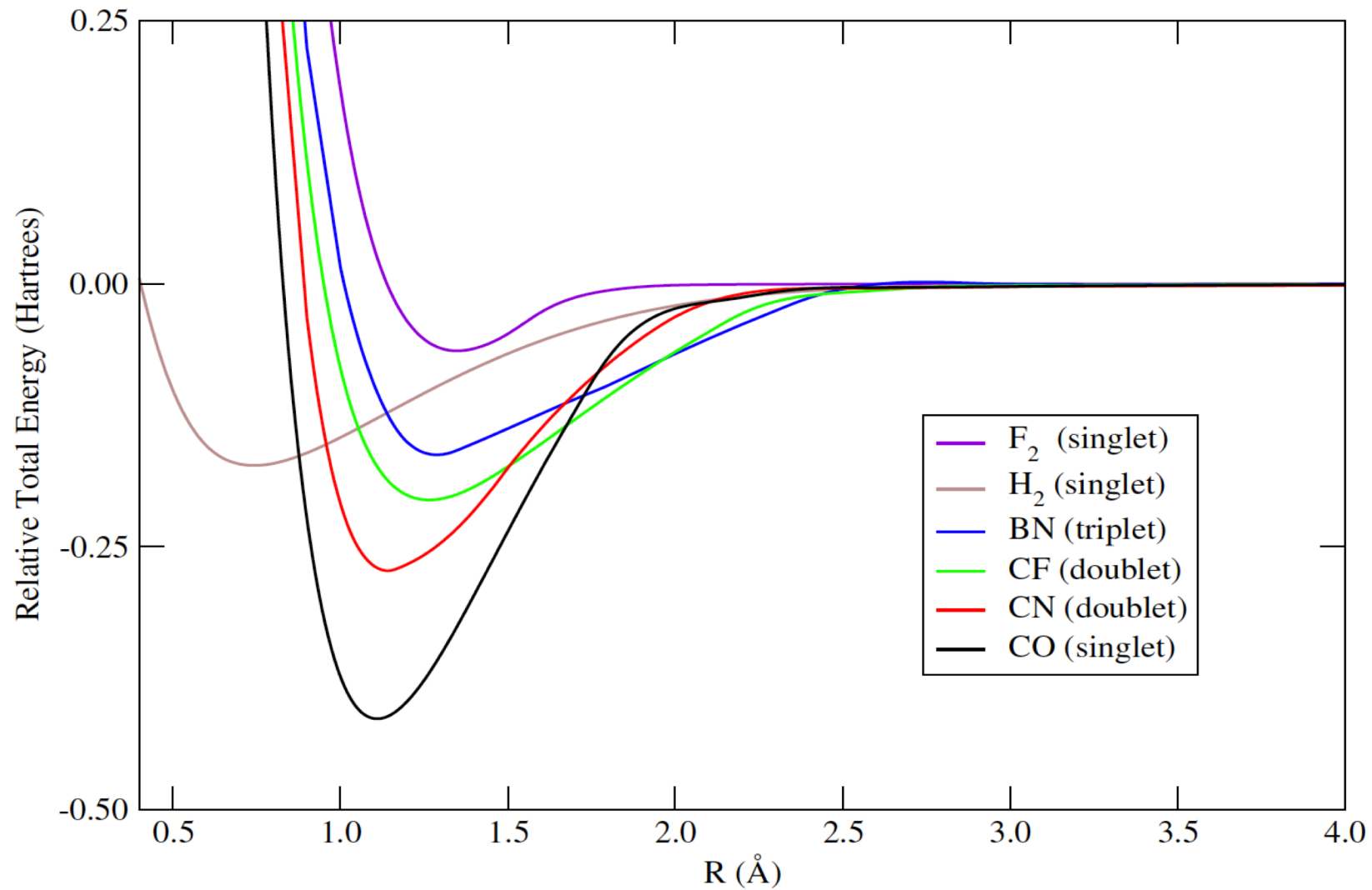
MAE (55)

30 mHa

8 mHa

-

Potential Energy Curves

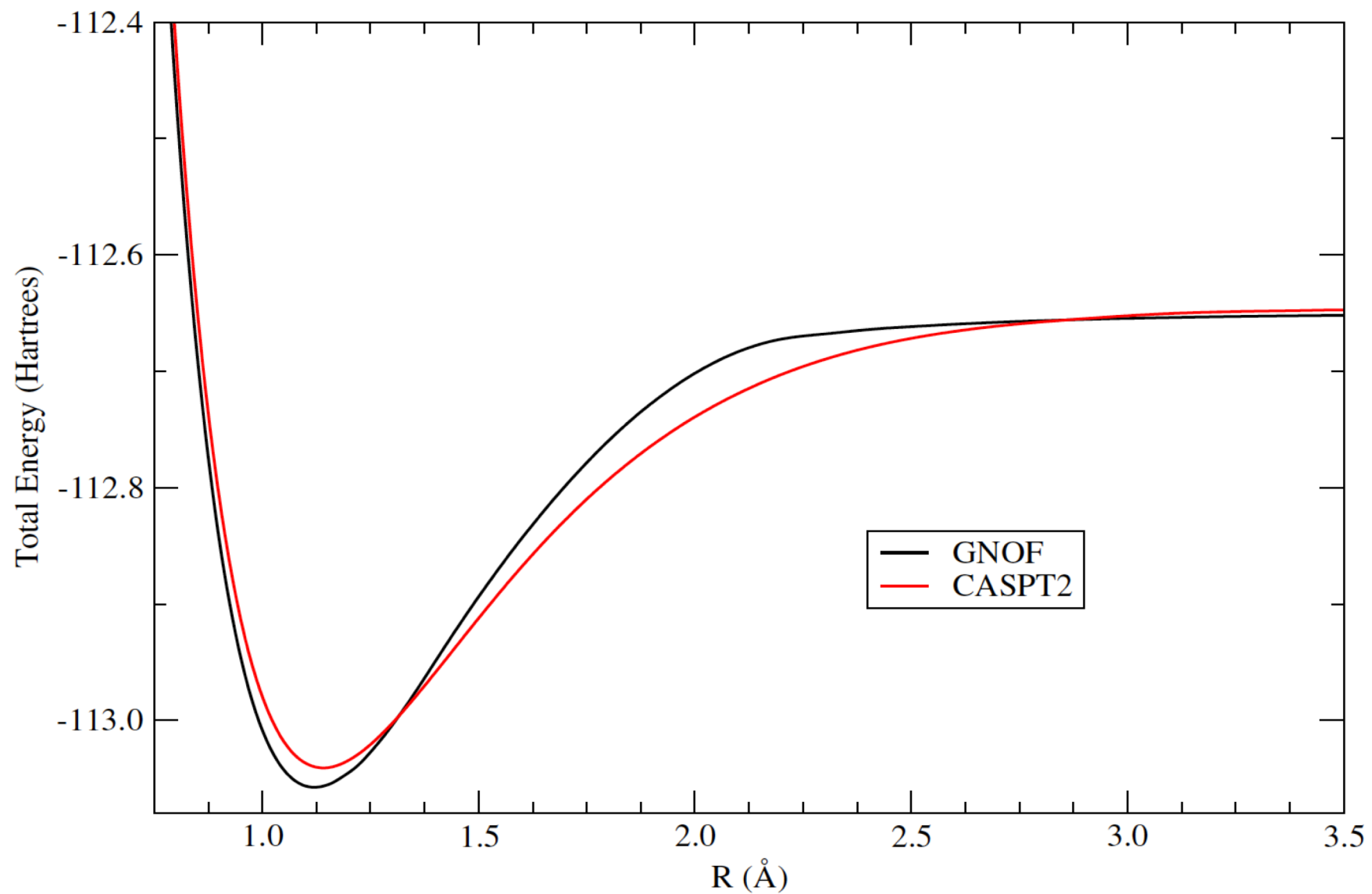


Comparison with the experimental data

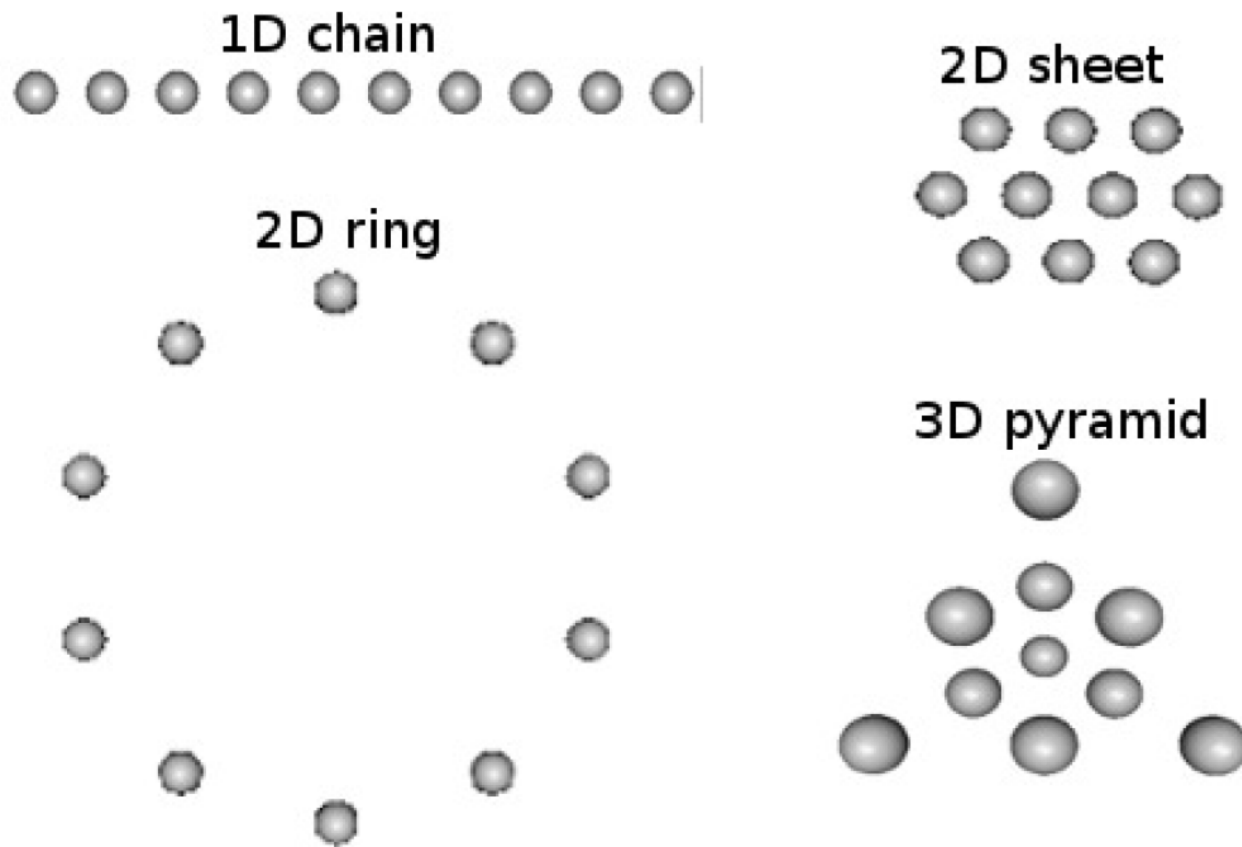
Mol	Mul	R_e	R_e^{exp}	D_e	D_e^{exp}	ω_e	ω_e^{exp}
F ₂	1	1.35	1.41	40.9	39.2	1212	917
H ₂	1	0.74	0.74	108.6	109.5	4404	4401
BN	3	1.29	1.32	102.3	94-133	1851	1515
CN	2	1.14	1.17	171.6	177.4	2344	2069
CF	2	1.26	1.27	129.0	128.7	1238	1308
CO	1	1.11	1.13	259.6	259.3	2391	2170

R_e (Å), D_e (kcal/mol), and ω_e (cm⁻¹)

PECs for the singlet ground state of the CO

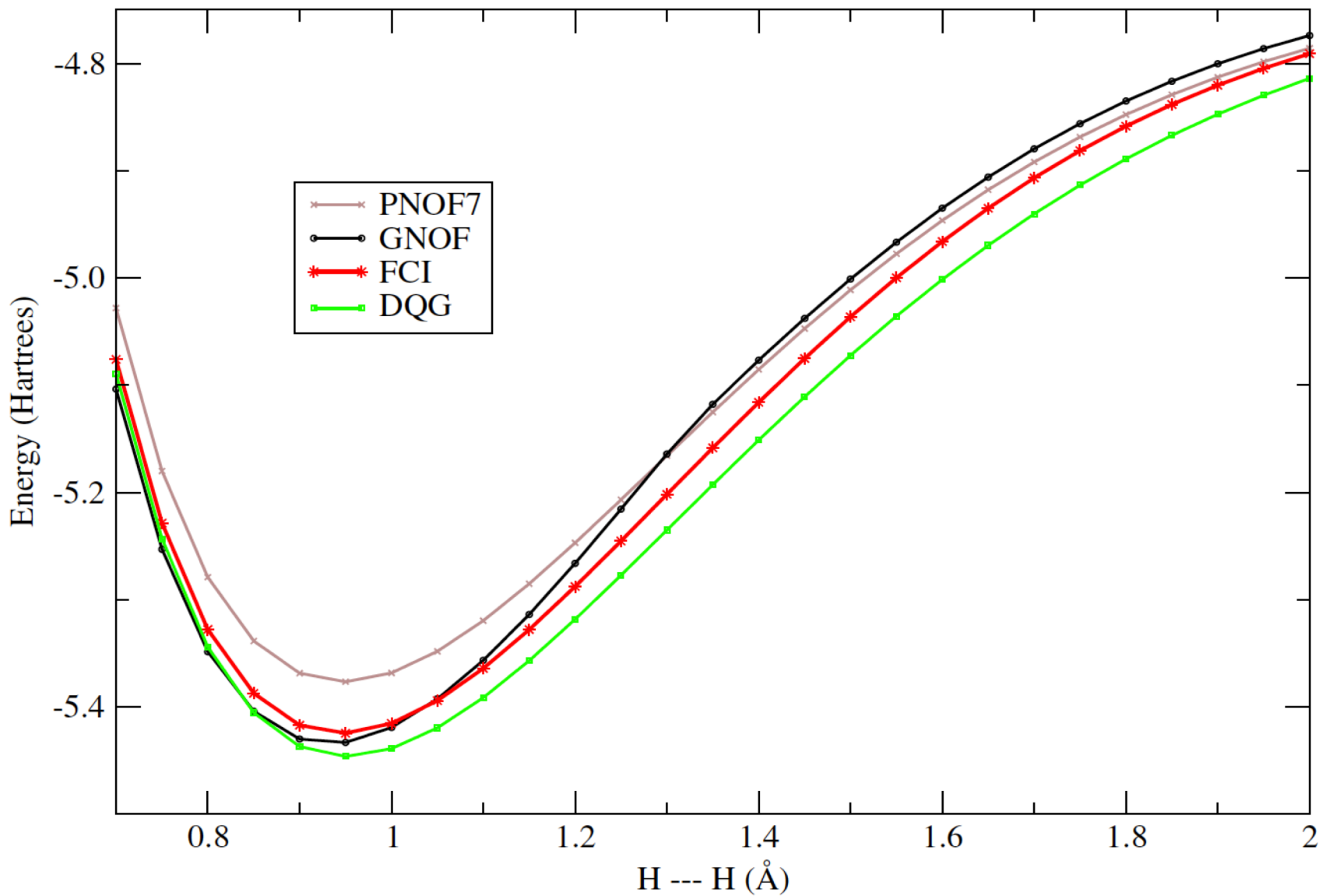


Benchmarking GNOF against FCI in one, two and three dimensions

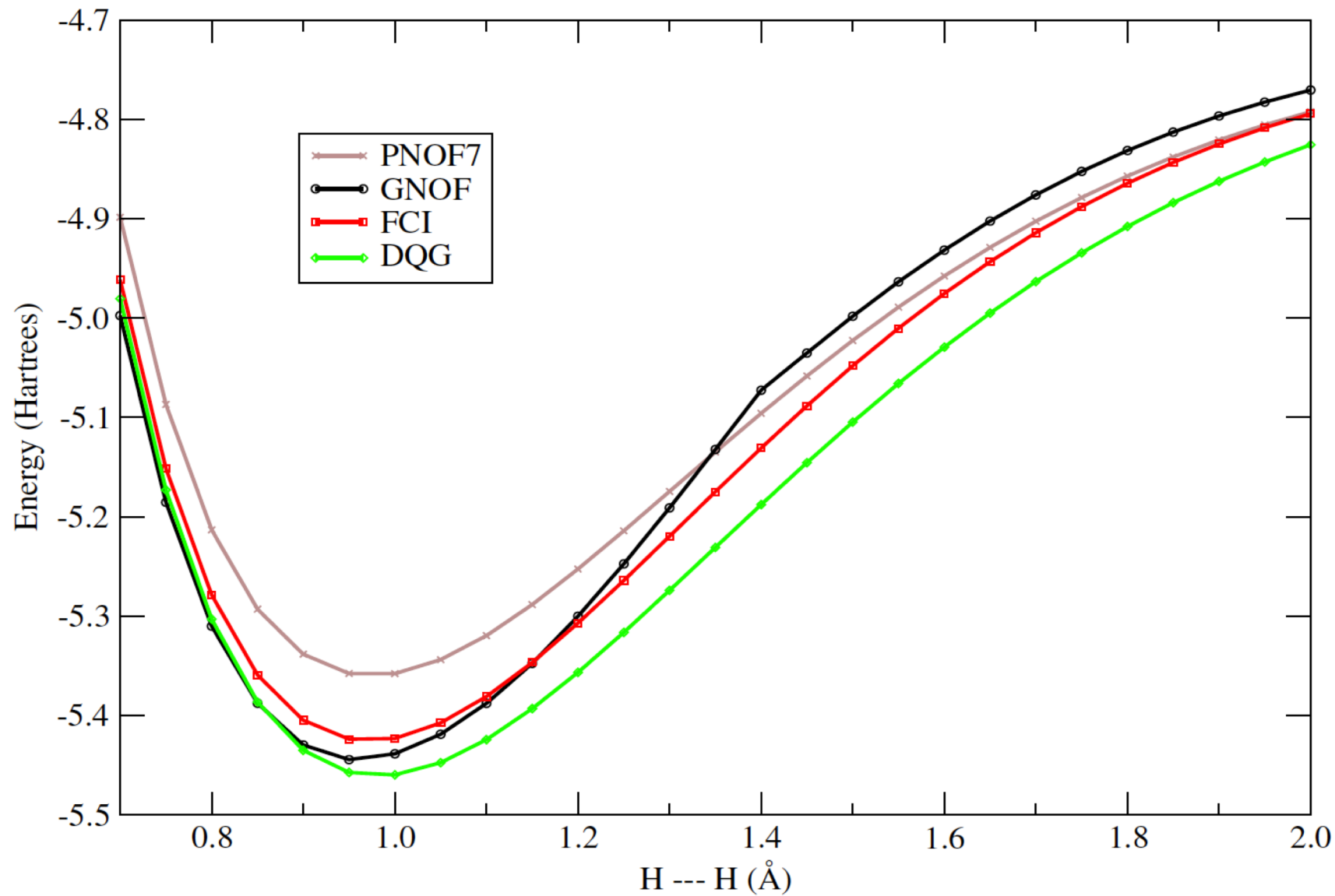


I. Mitxelena & M. Piris, J. Chem. Phys. 156, 214102 (2022)

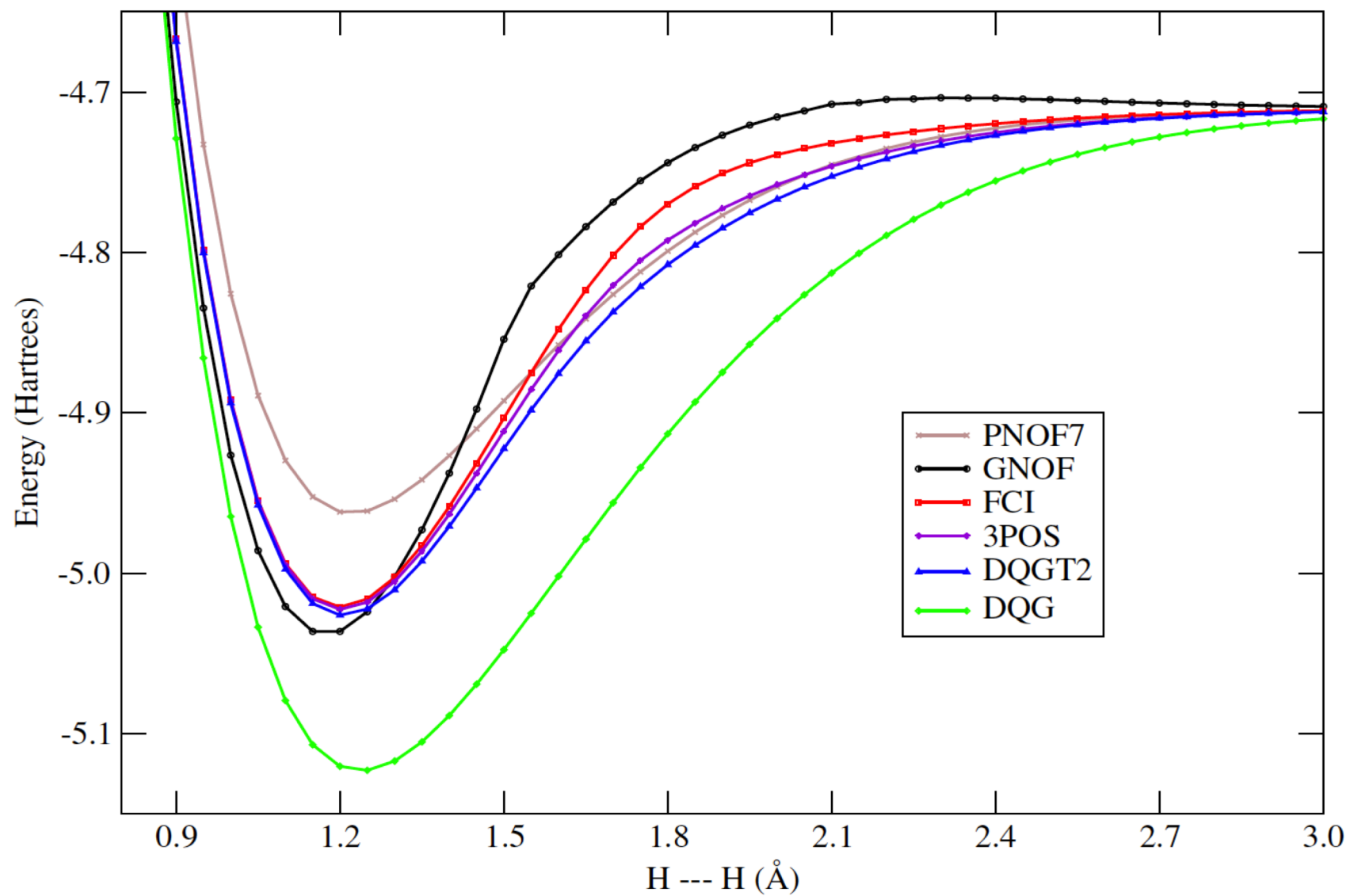
Dissociation curves corresponding to a **1D lineal chain** of 10 H



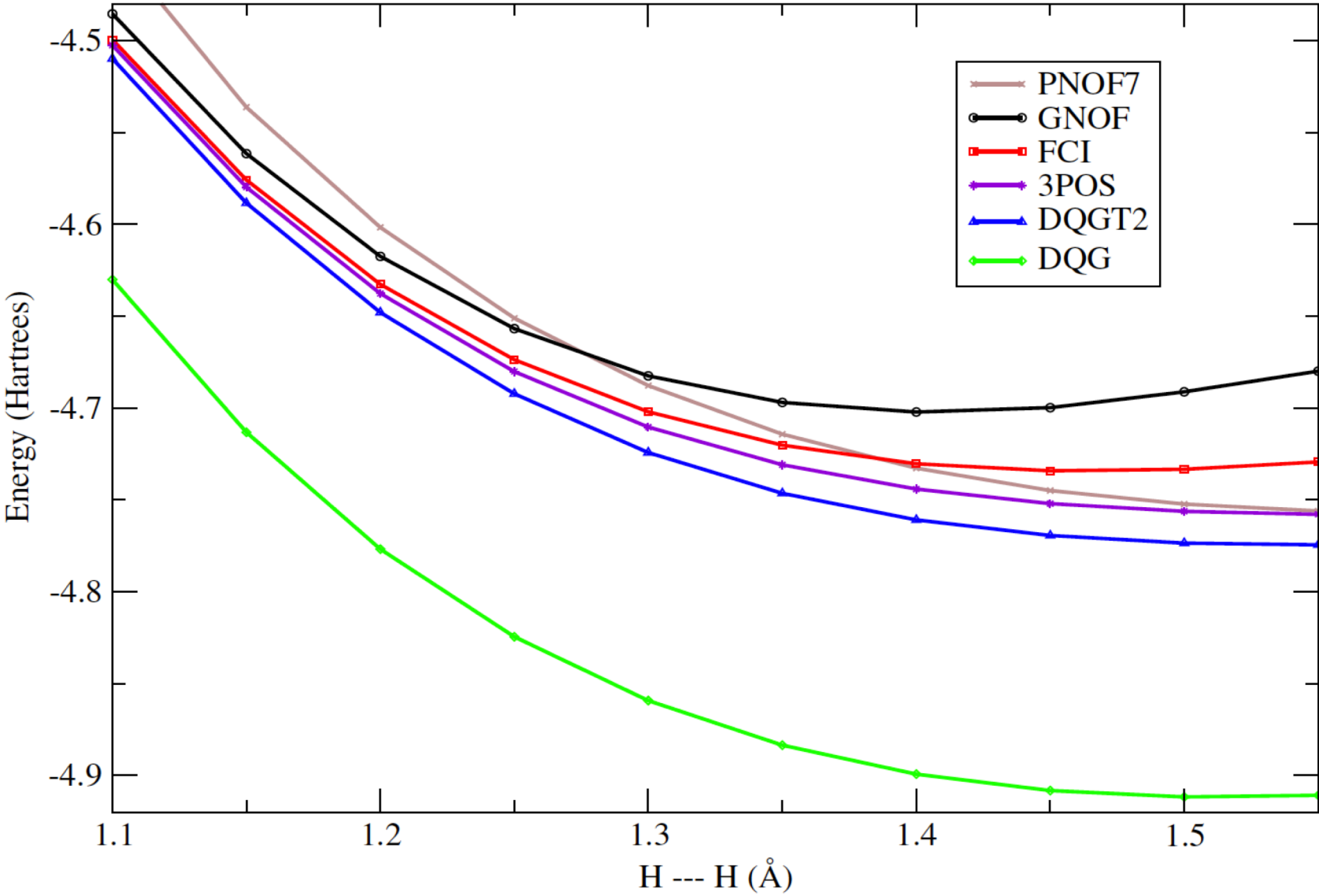
Dissociation curves corresponding to a 2D ring of 10 H



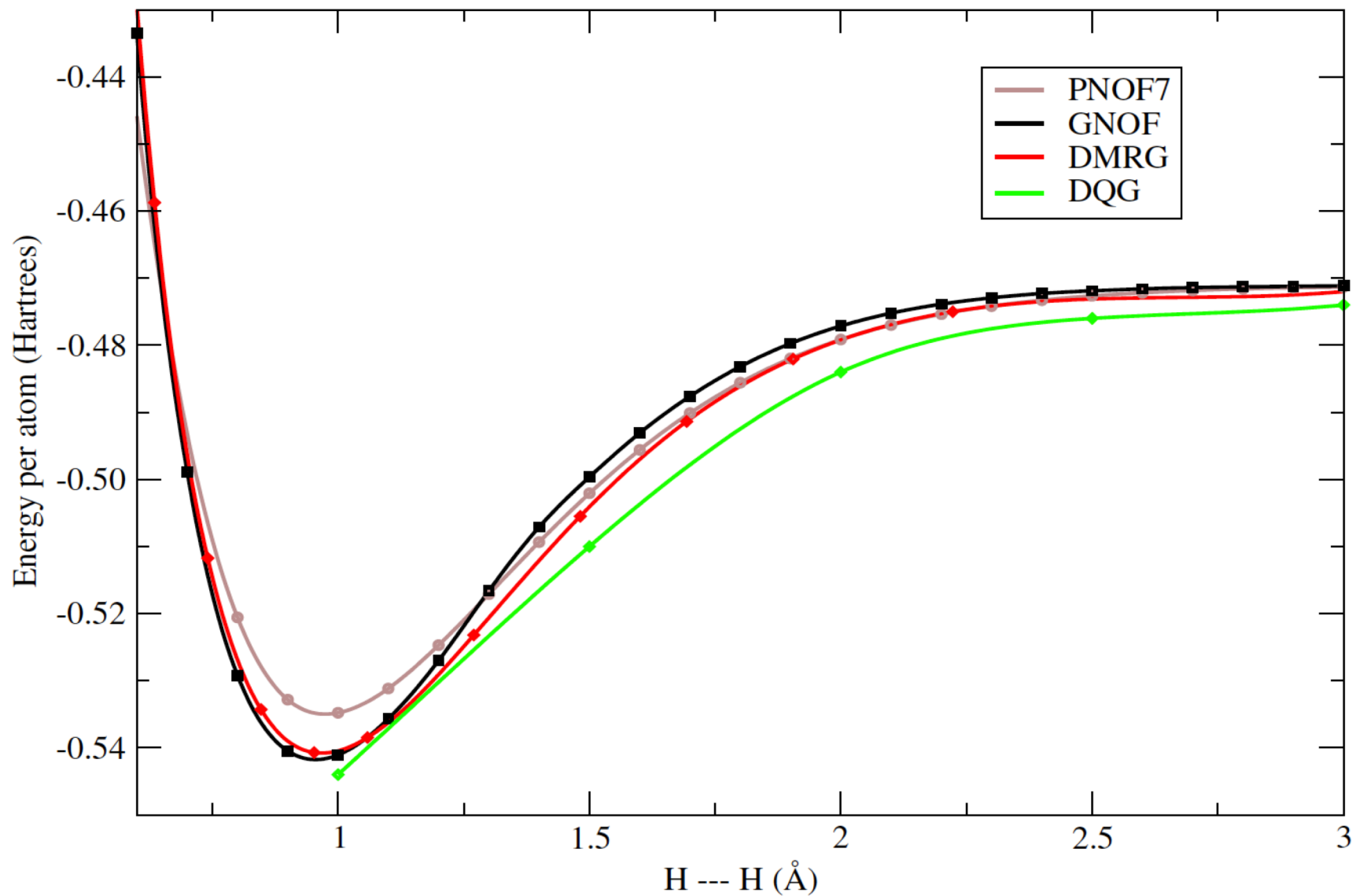
Dissociation curves corresponding to a 2D sheet of 10 H



Dissociation curves corresponding to a 3D pyramid of 10 H



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





Alejandro Rivero

Born-Oppenheimer Molecular Dynamics based on GNOF

- In **BOMD** calculations, the set of nuclei are propagated according to classical equations of motion, on the potential energy surface (PES) obtained by *on-the-fly* solution of the quantum-mechanical electronic structure problem

$$M_A \ddot{R}_A(t) = - \nabla_A E$$

$$E = E_{nuc} + E_{el} = \sum_{A < B} \frac{Z_A Z_B}{R_{AB}} + E_{el}$$

$$E_{el} = \sum_i n_i \mathcal{H}_{ii} + V_{ee} [N, \{n_i\}, \{\phi_i(\mathbf{x})\}]$$

- **BOMD** is, by definition, the true classical dynamics on the BO PES, assuming that the electronic problem is solved exactly (within a given model chemistry) at each time step
- Energy conservation is clearly a desirable feature

$$\text{MO-LCAO: } \phi_i(\mathbf{x}) = \sum_{\nu} C_{\nu i} \zeta_{\nu}(\mathbf{x}), \quad E_{el} = \sum_{\mu\nu} \Gamma_{\mu\nu} \mathcal{H}_{\mu\nu} + \sum_{\mu\nu\eta\delta} D_{\mu\eta\nu\delta} \langle \mu\eta | \nu\delta \rangle$$

The analytic energy gradients with respect to nuclear motion

$$\frac{dE}{dx_A} = \frac{\partial E_{el}}{\partial x_A} + \frac{\partial E_{nuc}}{\partial x_A} + \sum_{\mu j} \frac{\partial E_{el}}{\partial C_{\mu j}} \frac{\partial C_{\mu j}}{\partial x_A} + \sum_i \frac{\partial E_{el}}{\partial n_i} \frac{\partial n_i}{\partial x_A}$$

$$\sum_{\mu j} \frac{\partial E_{el}}{\partial C_{\mu j}} \frac{\partial C_{\mu j}}{\partial x_A} = - \sum_{\mu\nu} \lambda_{\mu\nu} \frac{\partial \mathcal{S}_{\mu\nu}}{\partial x_A}, \quad \lambda_{\mu\nu} = \sum_{ij} C_{\mu j} \lambda_{ji} C_{\nu i} \quad (\text{density force})$$

$$\sum_i \frac{\partial n_i}{\partial x_A} = 0 \rightarrow \sum_i \frac{\partial E_{el}}{\partial n_i} \frac{\partial n_i}{\partial x_A} = \mu \sum_i \frac{\partial n_i}{\partial x_A} = 0.$$

$$\frac{dE}{dx_A} = \sum_{\mu\nu} \Gamma_{\mu\nu} \frac{\partial \mathcal{H}_{\mu\nu}}{\partial x_A} + \sum_{\mu\nu\eta\delta} D_{\mu\eta\nu\delta} \frac{\partial \langle \mu\eta | \nu\delta \rangle}{\partial x_A} + \frac{\partial E_{nuc}}{\partial x_A} - \sum_{\mu\nu} \lambda_{\mu\nu} \frac{\partial \mathcal{S}_{\mu\nu}}{\partial x_A}$$



$E_k = 0.056 \text{ eV}$

$\Delta t = 0.2 \text{ ps}$

$R_{\text{ini}} = 10 \text{ \AA}$



Speed 16x



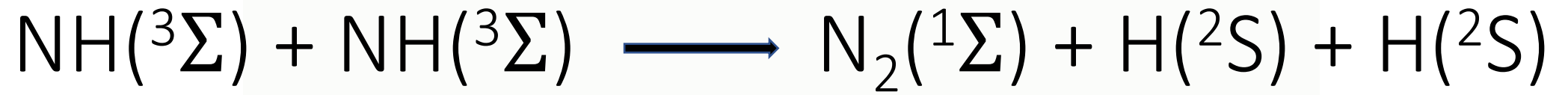
$E_k = 7.7 \text{ eV}$

$\Delta t = 0.5 \text{ ps}$

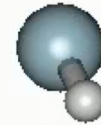
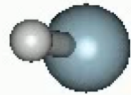
$R_{\text{ini}} = 10 \text{ \AA}$



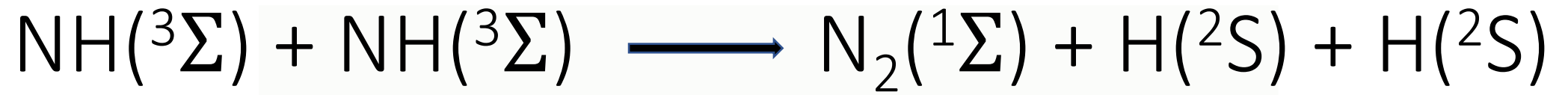
Speed 16x



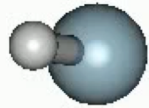
dt = 1 fs
R_{ini} = 10 Å



Speed 2x



$dt = 1\text{fs}$
 $R_{\text{ini}} = 10 \text{ \AA}$



Speed 2x

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/>

TAKE-HOME MESSAGES

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

Thank you for your attention !!!