Water, soft matter and reactions in solution: major challenges to microscopic modeling and simulation

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Advanced Modeling of Ions in Solutions, on Surfaces, and in Biological Environments

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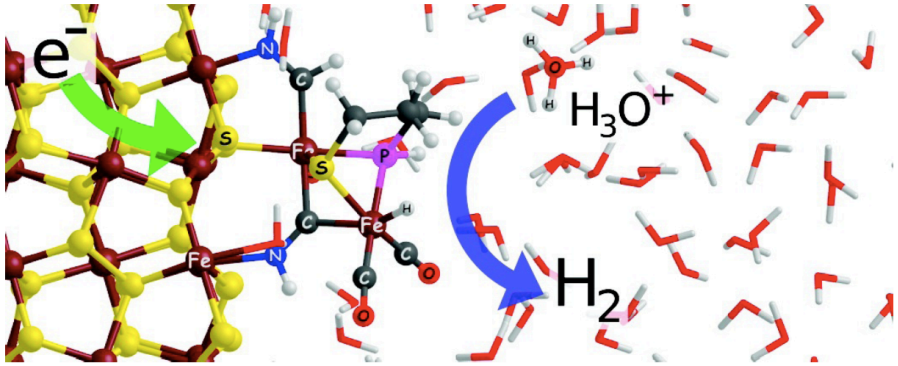

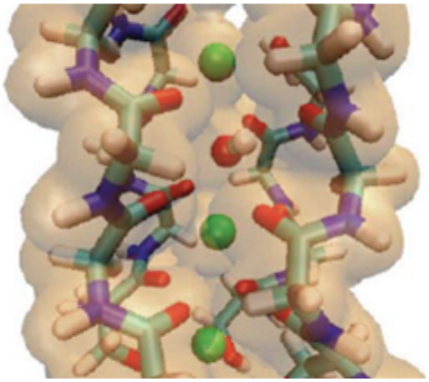

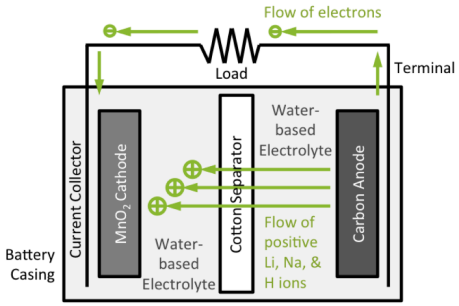

The AMIS team

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Electronic structure, ab-initio molecular dynamics, spectral properties

- **The Standard Model**

Density functional theory for ground–state electronic structure

GW-BSE for electronic excitation and spectral properties (photoemission, optical, uv, x-ray absorption…)

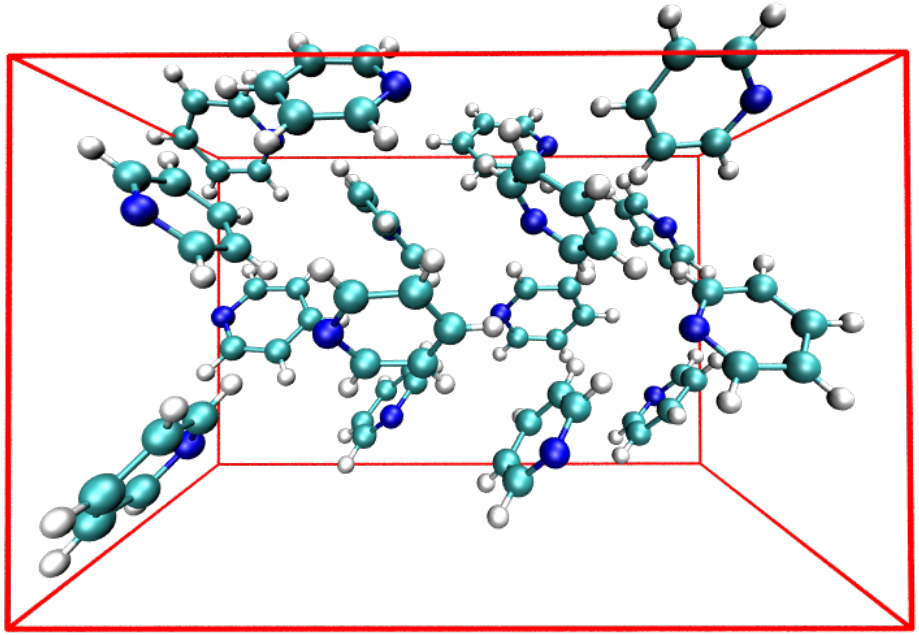
- **Beyond the Standard Model**

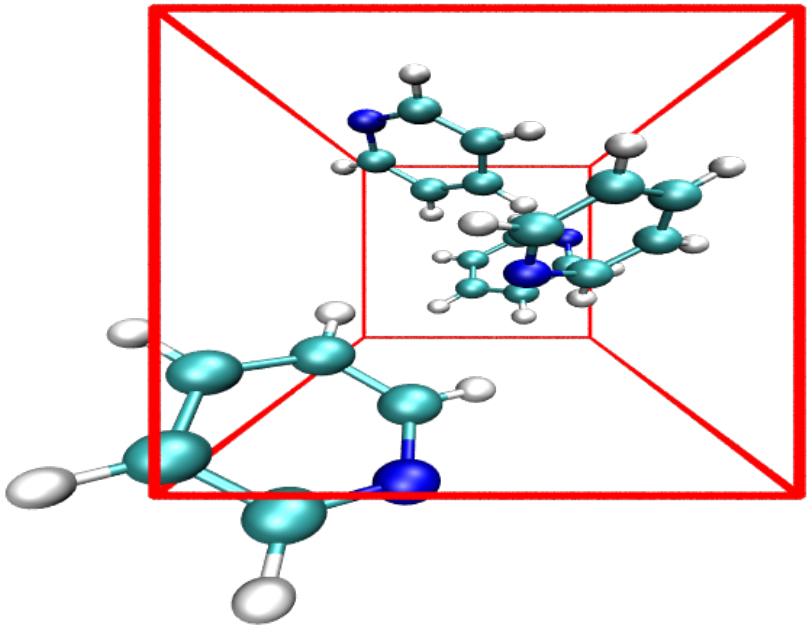
Weak interactions (H-bonding, vdW)

DFT functionals must be enhanced to model vdW interactions (an electron correlation effect)

H-bonding is described qualitatively correctly by common functionals but issues of accuracy remain (self-interaction error & overestimation of H-bond strength)

NPT Simulations of Pyridine Polymorphs





	h5-I (1 Bar) $Pna2_1$(Orthorhombic)				h5-II (1.1 GPa) $P2_12_12_1$(Orthorhombic)			
	0 K		153 K		0 K		293 K	
	Volume [Å^3]	Error	Volume [Å^3]	Error	Volume [Å^3]	Error	Volume [Å^3]	Error
Exp	--		1784		--		414	
PBE	2185	+22.5%	2250 ± 24	+26.1 %	442	+6.8 %	493 ± 8	+19.1 %
PBE+vdw	1710	- 4.2 %	1770 ± 22	- 0.7 %	396	- 4.3 %	414 ± 7	+0.01 %

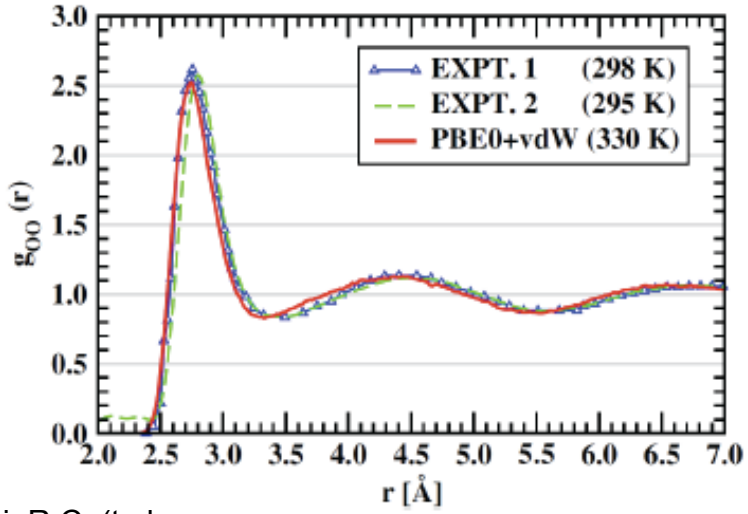
vdW functional: Tkatchenko, Scheffler, *PRL* (2009*);* Tkachenko, DiStasio, Car, Scheffler, *PRL* (2012)

From H-Y Ko, R. DiStasio, RC (to be published)

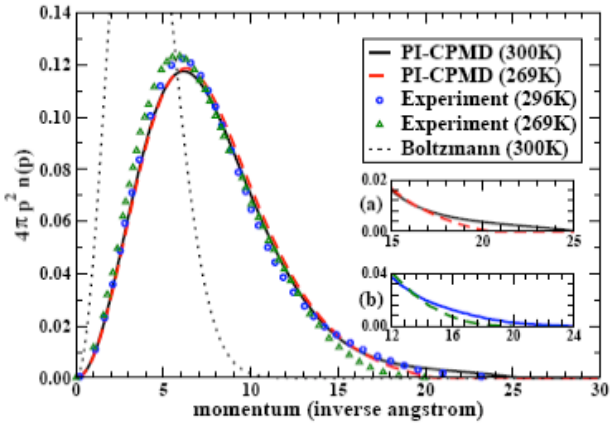
Water: DFT approximation, quantum nuclei

$(H_2O)_N$	PBE (330K)	PBE+vdW (330K)	Expt.
32	0.78 (40 ps)	0.98 (50 ps)	-
64	0.80 (40 ps)	0.98 (30 ps)	-
128	0.79 (30 ps)	0.99 (20 ps)	0.99
ice	0.97	1.01	0.93

Table : Densities (in g/cm^3) resulting from AIMD-NPT simulations of liquid water at the PBE and PBE+vdW levels of theory. All simulations were run using $E_0 = 130Ry$ ($E_{cut} = 150Ry$). The simulation temperature was set to $T = 330K$ to *approximately* account for NQE.



From B. Santra, R. DiStasio, Z. Li, R.C. (to be published)

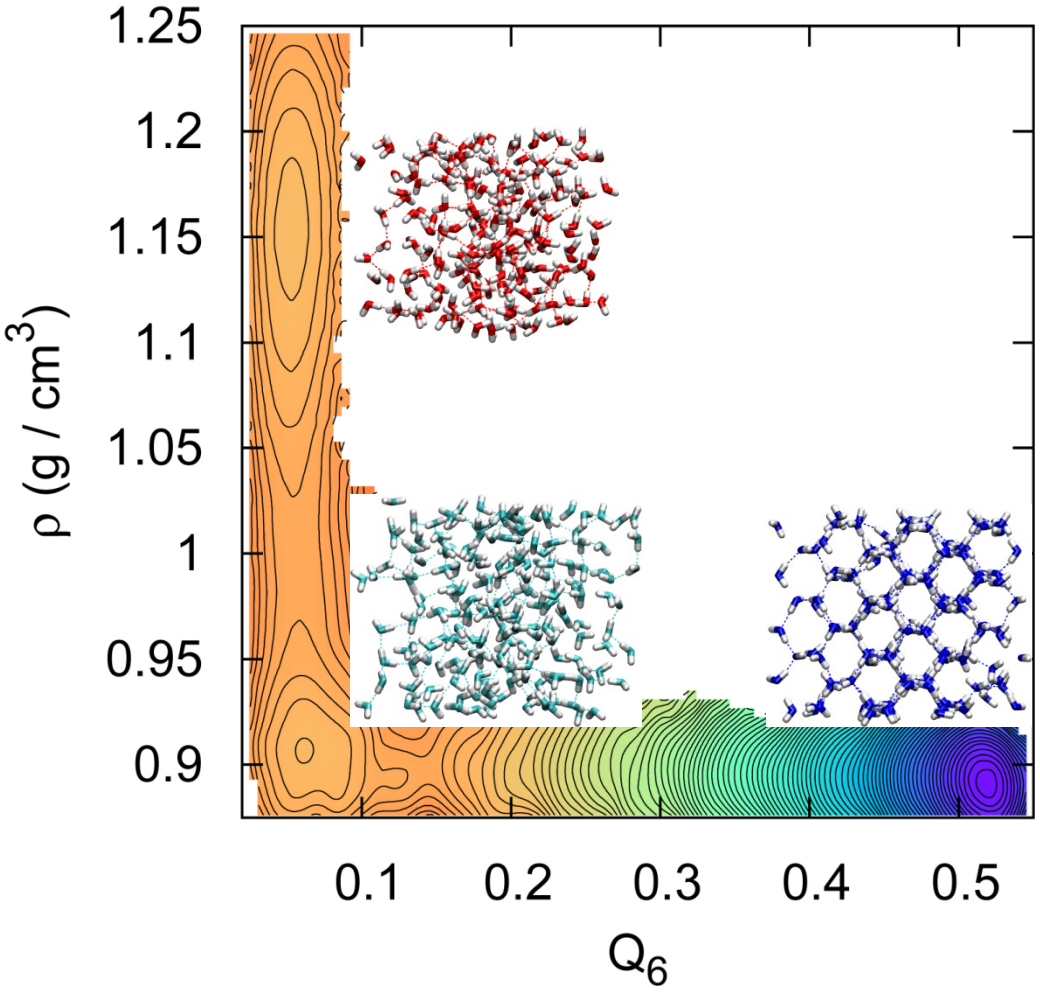


J.Morrone, R.C., *PRL* (2008)

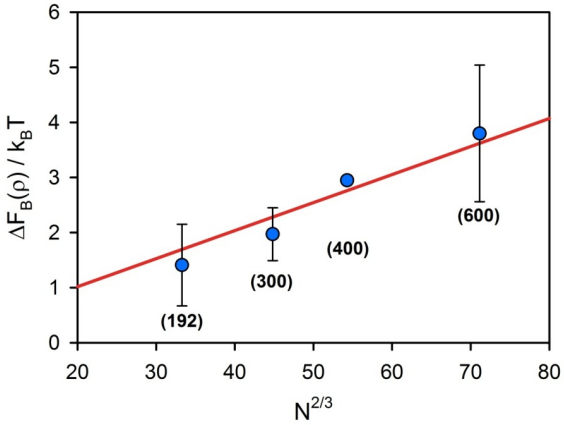
Soon we will start extensive PI-AIMD simulations on BG-Q (ALCC grant) using PBE0+vdW and color noise thermostats (Ceriotti, Parrinello); very effective parallelization

Anomalies, Phase diagram, Sampling Issues

- Secondary critical point (HDL-LDL transition)
- Is the transition genuinely first-order?



Finite size scaling with well tempered metadynamics



J. Palmer, R. Car, P. Debenedetti, Faraday Discuss, (2013)

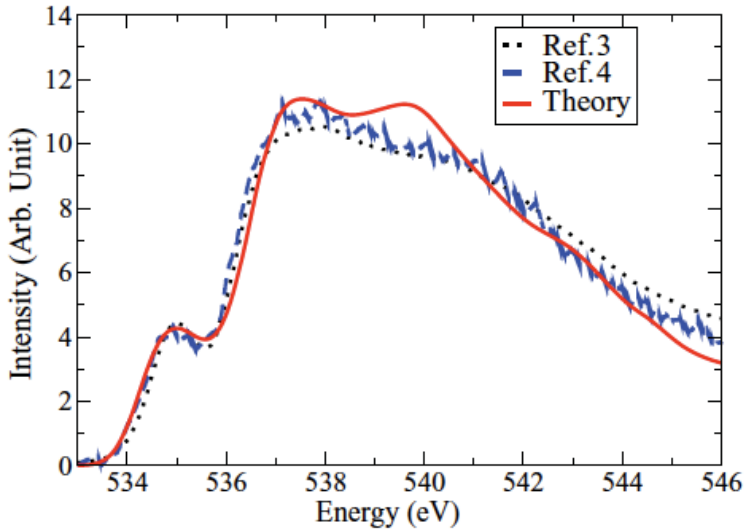
The large scale challenge

Collaboration with FASTMATH on Pole Expansion and Selected Inversion Method for Accelerating Electronic Structure Calculations

Electron excitations

GW-BSE + good sampling of disordered structures

Ionization potential of water ions (poster by C.W. Swartz and X. Wu, Temple)



x-ray absorption spectra of liquid water (GW: static COHSEX) (L. Kong, X. Wu, R.C. *PRB (*2012))

DFT Issues

- Functional fix not always works, plethora of functionals, no systematic procedure for improving
- Self-interaction error may cause severe difficulties, for example in the case of the water radical OH and in general when dealing with chemical reactions
- Incorrect dissociation of molecules into non-interacting fragments (“static” or strong correlation)

Occupation Probabilities-Natural Orbital Functional Theory

$$E = \langle \Psi | H | \Psi \rangle = Tr[H\pi]$$

$$\Psi(x_1, x_2, \ldots, x_N) = \sum_{\mathbf{n}} C_{\mathbf{n}} \Phi_{\mathbf{n}}(x_1, x_2, \ldots, x_N) \qquad (\mathbf{n} \equiv n_1 n_2 .. n_{N/2})$$

Simplest version: Doubly Occupied NO states – seniority 0 (DOCI)

$$\pi(x_1', x_2'; x_1, x_2) = N(N-1) \int dx_3 \cdots dx_N \Psi(x_1', x_2', \cdots, x_N) \Psi^*(x_1, x_2, \cdots, x_N),$$

OP-NOFT: R Gebauer, MH Cohen, R.C.

$$E = 2\sum_i h_{ii} p_1(i) + \sum_{ij} p_{11}(ij)\Big[2J_{ij} - K_{ij}\Big] + \sum_{i\neq j} p_{10}^{1/2}(ij)\, p_{01}^{1/2}(ij)\, s(i)s(j)\xi(ij)K_{ij}$$

$$J_{ij} \equiv \langle \varphi_i\varphi_j | v | \varphi_i\varphi_j \rangle = \int d\mathbf{r}_1\, d\mathbf{r}_2 \frac{\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)}{r_{12}}$$

$$K_{ij} \equiv \langle \varphi_i\varphi_j | v | \varphi_j\varphi_i \rangle = \int d\mathbf{r}_1\, d\mathbf{r}_2 \frac{\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)\varphi_j(\mathbf{r}_1)\varphi_i(\mathbf{r}_2)}{r_{12}}$$

$$0 \le \xi(ij) \le 1$$

$$p_1(k) \equiv \sum_{\mathbf{n}} C_{\mathbf{n}}^2 \nu_{k,\mathbf{n}} \qquad p_{11}(ij) \equiv \sum_{\mathbf{n}} C_{\mathbf{n}}^2 \nu_{i,\mathbf{n}}\nu_{j,\mathbf{n}} \qquad p_{10}(ij) \equiv \sum_{\mathbf{n}} C_{\mathbf{n}}^2 \nu_{\mathbf{n},i}(1-\nu_{\mathbf{n},j})$$

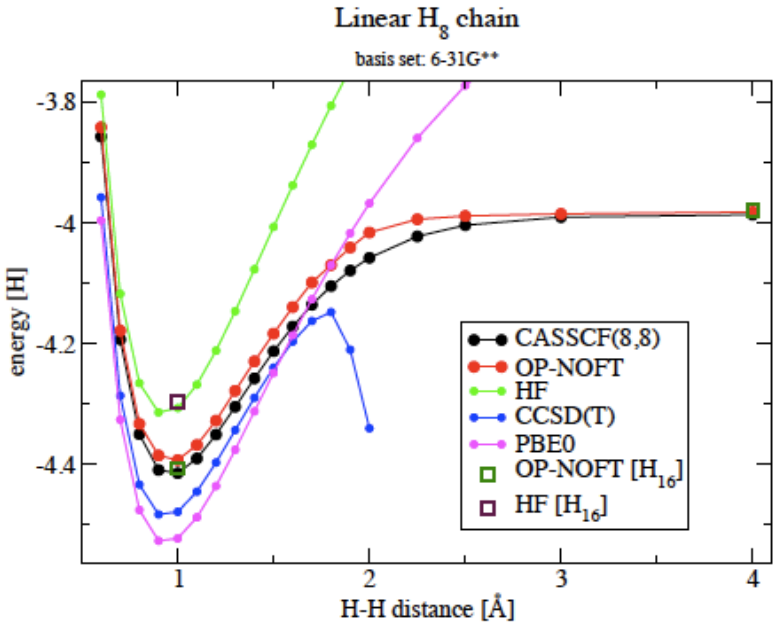
$$p_1(i) = p_{11}(ij) + p_{10}(ij)$$

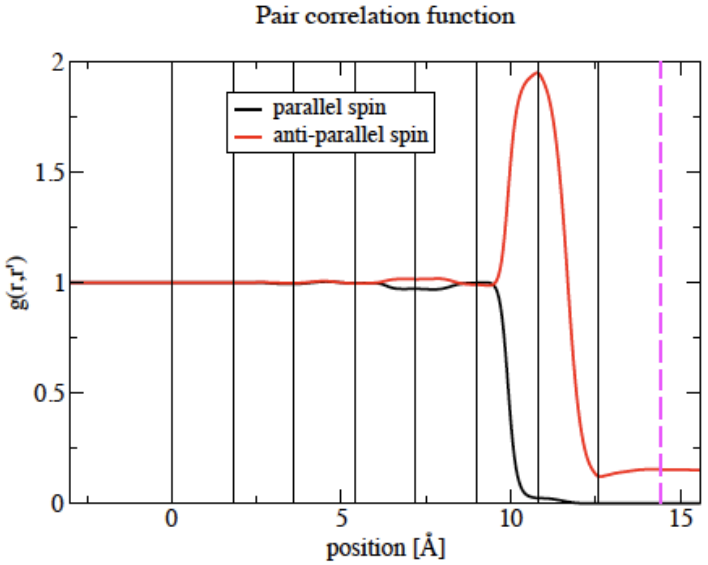
$$\xi(ij) \simeq F[p_{11}] \quad \text{while exact } \xi(ij) = F[p_{11\ldots1}]$$

p_1, p_{11} satisfy bounds and sum rules to ensure N-representability

The ground-state energy is the infimum of E wrt $\varphi_i(\mathbf{r})$, $p_1(i)$, $p_{11}(ij)$ subject to constraints, bounds and sum rules

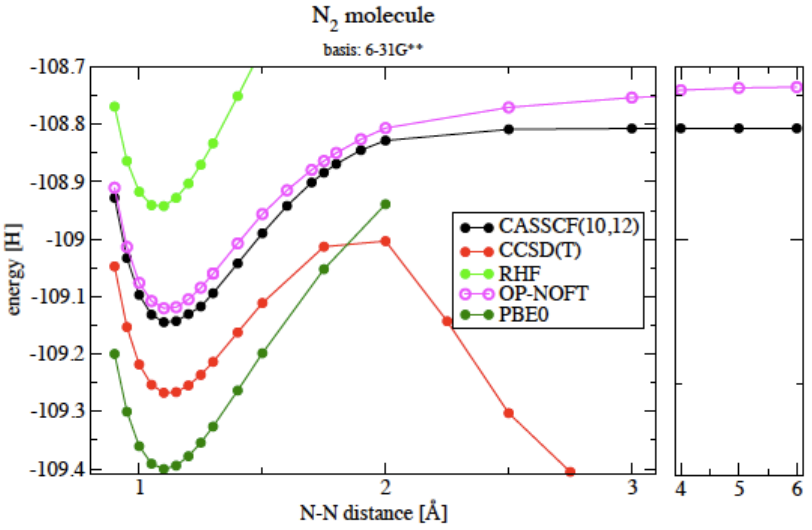
Minimization of E has the same scaling with N of Hartree-Fock theory



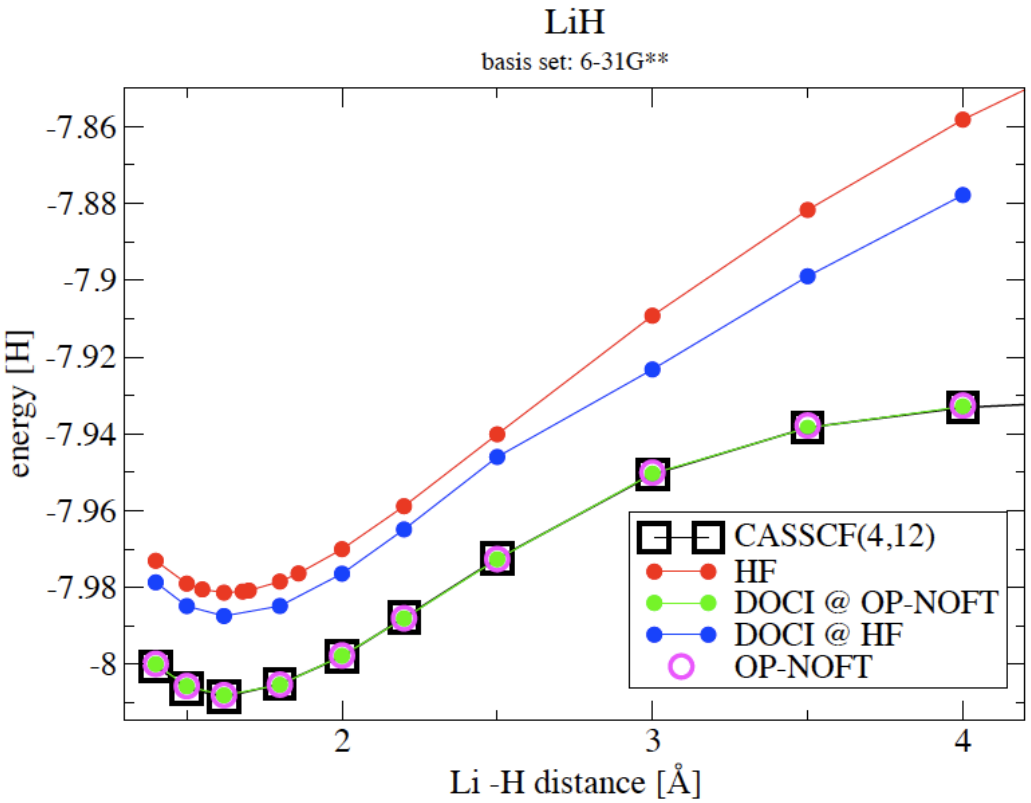


$$\int d\mathbf{r}_2 \; \pi(\mathbf{r}', \mathbf{r}_2; \mathbf{r}, \mathbf{r}_2) = (N-1)\rho(\mathbf{r}, \mathbf{r}') \text{ and}$$

$$\int d\mathbf{r}_1 \, d\mathbf{r}_2 \; \pi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) w(r_{12}) \geq 0,$$



OP-NOFT vs DOCI



DOCI: Weinhold and Bright Wilson (1967)

- Calculation of forces, structural optimization and AIMD "straightforward"

- This version of the theory (corresponding to DOCI) includes only *intra-shell* correlations among electrons of opposite spins

- A more accurate version including also *inter-shell* correlations among electrons of arbitrary spin is possible: the scaling would still be polynomial but worse than HF

Concluding Remarks

SIZE, TIME (SAMPLING), ACCURACY are all very important issues in molecular simulations

The goal of chemical accuracy in condensed phase simulations can be within reach, by combining physics theory, effective algorithms and high performance computer platforms