

PNOF5: A new benchmark tool in computational chemistry

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Outline

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Challenges for theoretical and computational chemistry

Goal: Solve $H\Psi = E\Psi$

Accuracy

- DFT/DMFT: Improving functionals.
- WFN: Improving the approximation of the WFN.

Feasibility

- Toward linear scaling

Interpretation and analysis

- Something else than numbers?

Preamble

Goal: Solve $H\Psi = E\Psi$

Ansatz $F(\Psi, \rho, \gamma, \text{etc.})$

		<i>Ansatz $F(\Psi, \rho, \gamma, \text{etc.})$</i>	
		EXACT	APPROX.
$E(F)$	EXACT	FCI	HF, CI, CAS CC, MPn, ...
	APPROX.	DFT, DMFT	semiempirics PNOF5

This classification does NOT reflect accuracy!

Preamble

Goal: Solve $H\Psi = E\Psi$

HF	N^3
DFT	N^{3-4}
MP2	N^5
CISD	N^6
CCSD(T)	N^7 (Standard gold)

- Systems in which correlation effects are very important. (Cr_2 , CH_5^+)
- Benchmarking tool in computational chemistry.

Density Matrix Functional Theory (DMFT)

The *exact* functional of the energy can be written in terms of the first-order density matrix [$\mathbf{1} \equiv (\vec{x}_1, s_1)$]:

$${}^1D(\mathbf{1}'|\mathbf{1}) = \sum_{ij} D_{ij} \phi_i^*(\mathbf{1}') \phi_j(\mathbf{1})$$

The energy is known as an explicit functional of 1-RDM and 2-RDM ($E[N, {}^1\mathbf{D}, {}^2\mathbf{D}]$). The DMFT attempts the calculation entirely from 1-RDM

$$E = E[N, {}^1\mathbf{D}] = h[N, {}^1\mathbf{D}] + V_{ee}[N, {}^1\mathbf{D}]$$

by reconstruction

$$E[N, {}^1\mathbf{D}] \rightarrow E[N, {}^1\mathbf{D}, {}^2\mathbf{D}]$$

Gilbert TL, PRB 12, 2111 (1975)

Levy M, PNAS 76, 6062 (1979)

Natural Orbital Functional Theory (NOFT)

The 1-RDM can be diagonalized to give natural orbitals:

$${}^1D(\mathbf{1}'|\mathbf{1}) \rightarrow \sum_i n_i \eta_i^*(\mathbf{1}') \eta_i(\mathbf{1})$$

so that the functional it is even simpler

$$E[N, \{\phi_i, n_i\}] \rightarrow E[N, {}^1\mathbf{D}] \rightarrow E[N, {}^1\mathbf{D}, {}^2\mathbf{D}]$$

actually you may write it as

$${}^2\mathbf{D} = {}^2\mathbf{D}[\{\phi_i, n_i\}]$$

or even

$$\Gamma = \Gamma[\{\phi_i, n_i\}]$$

where Γ is the second-order cumulant.

Piris Natural Orbital Functional Theory

The second-order cumulant:

$${}^2D_{pq,rt}^{\sigma\sigma,\sigma\sigma} = \frac{n_p^\sigma n_q^\sigma}{2} (\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr}) + \Gamma_{pq,rt}^{\sigma\sigma,\sigma\sigma}$$

$${}^2D_{pq,rt}^{\alpha\beta,\alpha\beta} = \frac{n_p^\alpha n_q^\beta}{2} \delta_{pr}\delta_{qt} + \Gamma_{pq,rt}^{\alpha\beta,\alpha\beta}$$

The PNOF consists on the approximation of the cumulant:

$$\Gamma_{pq,rt}^{\sigma\sigma,\sigma\sigma} = -\frac{\Delta_{pq}^{\sigma\sigma}}{2} (\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr})$$

$$\Gamma_{pq,rt}^{\alpha\beta,\alpha\beta} = -\frac{\Delta_{pq}^{\alpha\beta}}{2} \delta_{pr}\delta_{qt} + \frac{\Pi_{pr}}{2} \delta_{pq}\delta_{rt}$$

Δ and Π define the current PNOF approximation:

$$E^{\text{PNOF}} = E^{\text{PNOF}} [\{\phi_i, n_i\}, \Delta, \Pi]$$

PNOF5: Formula for singlet states

$$\Delta_{qp} = \begin{cases} n_p^2, & q = p \\ 0, & q \neq p \\ n_{\tilde{p}}n_p, & q = \tilde{p} \end{cases} \quad \Pi_{qp} = \begin{cases} n_p, & q = p \\ 0, & q \neq p \\ -\sqrt{n_{\tilde{p}}n_p}, & q = \tilde{p} \end{cases}$$

$$n_p + n_{\tilde{p}} = 1$$

$$E = \sum_p n_p [(2H_{pp} + J_{pp}) - \sqrt{n_{\tilde{p}}n_p}K_{p\tilde{p}}] + \sum''_{pq} n_p n_q (2J_{pq} - K_{pq})$$

$$\left(\sum'' : q \neq p, \tilde{p} \right)$$

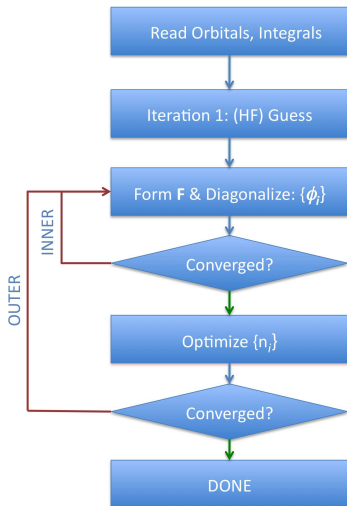
Piris *et al.*, *J. Chem. Phys.* 134, 164162 (2011)

PNOFid5: Implementation & Algorithm

The cost is driven by:

$$1. \mathbf{F} \leftarrow \mathbf{J}, \mathbf{K}$$

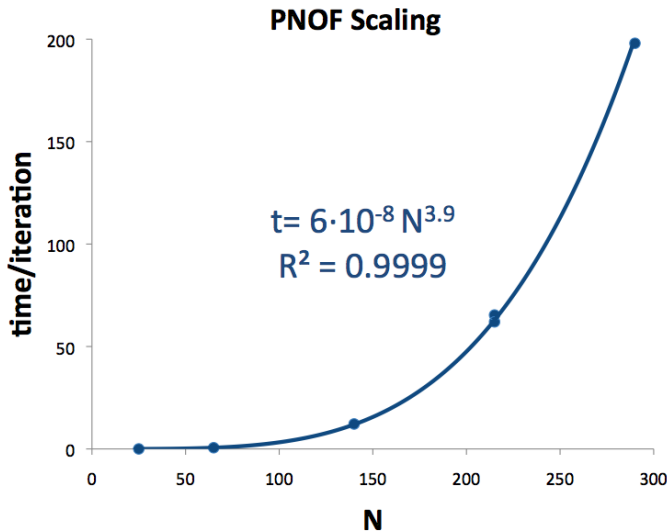
$$2. n_{it} = n_{it}^{out} \times n_{it}^{inn}$$



Piris M., Ugalde JM. JCC 30, 2078 (2009)

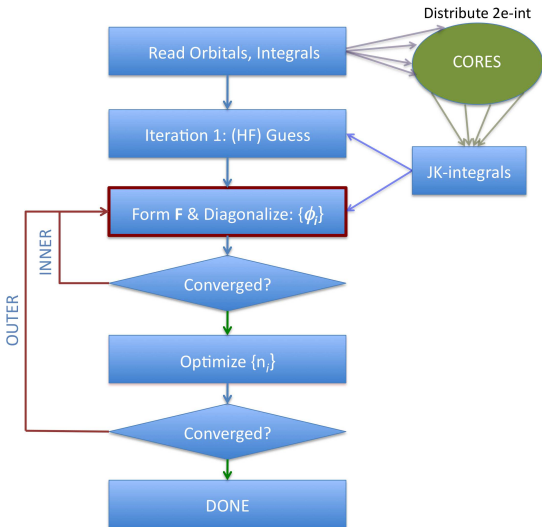
Piris M., **PNOFid5** (2011)

Computational cost of PNOF5

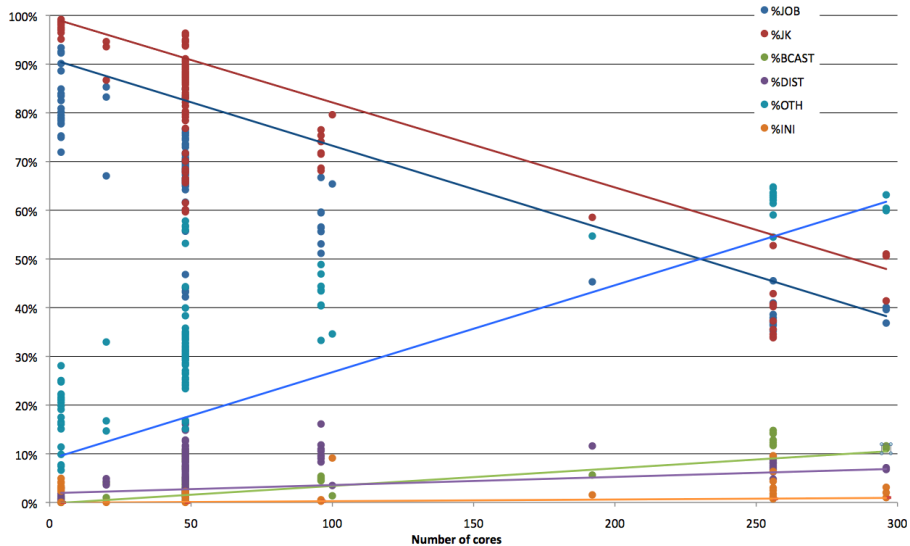


Overall cost is $\alpha n_{it} N^4$. Typically n_{it} is of the order of 1000.

MPI-PNOFid5: The MPI Algorithm



MPI-PNOFid5: Performance



MPI Performance

Calculation profile for a 512-core run:

- 40% Computation of JK-integrals (parallelized).
- 22% Computation of H_{core} .
- 23% Computation of the Gradient.
- 15% Calculation of F matrix.

These 60% is split into four different subroutines that can be parallelized to increase the efficiency.

A few examples

C-H and S-H dissociation energies (kcal/mol) in Cysteine.

	C-H	S-H
HF	187.32	192.06
MPWB1K	156.29	156.99
PNOF5	99.32	78.77
CASPT2	98.7*	85.08

C-H and O-H dissociation energies (kcal/mol) in Serine.

	C-H	O-H
MPWB1K	155.02	192.94
PNOF5	102.20	101.70
CASPT2	101.05	111.03

A few examples

19 small Molecular structures: HF, NH₃, CH₄, N₂

	CCD Frozen		CCD		CCT Frozen	
	Signed	Abs	Signed	Abs	Signed	Abs
Mean	1.53	2.10	1.60	2.20	0.41	1.33
dev	3.09	2.76	3.10	2.76	2.13	1.76
Max.		13.60		13.61		7.19

Summary

- PNOF5 accuracy lies between CASSCF and CASPT2. Good molecular structures.
- PNOF5 scales like N^4 time a large prefactor. Implementation of techniques for convergence acceleration is necessary.
- MPI-PNOF5 yields high efficiencies (75%) for up to 100 cores. Computations on 512 cores (40%) will be efficient upon further parallelization.
- After improvements the study of large molecules will be possible with PNOF5.

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