

NOF Theory of the molecular electronic structure

M. Piris^{1,2}, J. M. Matxain¹, F. Ruipérez¹,
X. Lopez¹, J. M. Ugalde¹, E. Matito³

¹Kimika Fakultatea, UPV/EHU, and DIPC, P.K. 1072, 20080 Donostia

²IKERBASQUE, Basque Foundation for Science, 48011 Bilbao

³Institute of Computational Chemistry, University of Girona, 17071 Girona

January 15, 2013



The electronic energy E for N -electron systems

$$E = \sum_{ik} H_{ik} \Gamma_{ki} + \sum_{ijkl} \langle ij|kl \rangle D_{kl,ij}$$

- Γ_{ki} : 1-RDM
- $D_{kl,ij}$: 2-RDM
- H_{ik} : core-Hamiltonian
- $\langle ij|kl \rangle$: Coulomb integrals

$E[N, \Gamma, \mathbf{D}]$ is an explicitly known functional of the 1- and 2-RDMs!

Variational Methods:

$$DFT \quad (\text{reconstruction}) \quad RDMs \quad (\text{contraction}) \quad CI, MCSCF, \\ \rho(\mathbf{r}) \implies \Gamma, D \quad \longleftarrow \Gamma^N \longleftarrow \Psi \quad CCSD, \dots$$

Advantages of Natural Orbital Functional Theory:

- the necessary and sufficient conditions for the N-representability of the 1-RDM are easily implementable.
- the kinetic energy is explicitly defined and does not require the construction of a functional. Remains only to find approximation for the electron-electron functional V_{ee} .
- NOFT allows us now to make calculations on challenging systems with high degree of accuracy at reasonable computational cost.

Outline

- 1 Introduction to the NOFT
 - Reconstructive functional: PNOF
- 2 Solving the system of equations
 - computational efficiency of the method
- 3 Results and chemical accuracy
 - examples of systems, where DFT yields pathological failures
 - potentiality of the NOF theory
- 4 orbital representations
- 5 Closing Remarks

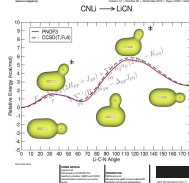
PCCP

Physical Chemistry Chemical Physics

View Article Online

DOI: 10.1039/b712469h

This journal is © the Royal Society of Chemistry 2007



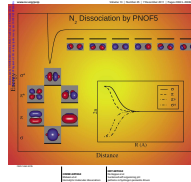
PCCP

Physical Chemistry Chemical Physics

View Article Online

DOI: 10.1039/b712469h

This journal is © the Royal Society of Chemistry 2007



1-RDM Functional

Last term in the Energy: $U[N, \mathbf{D}] = \sum_{ijkl} \langle ij|kl \rangle D_{kl,ij}$ can be replaced by an unknown functional of the 1-RDM:

$$V_{ee}[N, \Gamma] = \min_{\mathbf{D} \in \mathbf{D}(\Gamma)} U[N, \mathbf{D}]$$

$\mathbf{D}(\Gamma)$: family of N-representable 2-RDMs which contract to the Γ

$$E[N, \Gamma, \mathbf{D}] \Rightarrow E[N, \Gamma] = \sum_{ik} H_{ik} \Gamma_{ki} + V_{ee}[N, \Gamma]$$

T. L. Gilbert, Phys. Rev. B 12, 2111 (1975); M. Levy, Proc. Natl. Acad. Sci. U.S.A. 76, 6062 (1979)

Natural Orbital Functional

The 1-RDM can be diagonalized by a unitary transformation of the spin-orbitals $\{\phi_i(\mathbf{x})\}$:

$$\Gamma_{ki} = n_i \delta_{ki}, \quad \Gamma(\mathbf{x}'_1 | \mathbf{x}_1) = \sum_i n_i \phi_i(\mathbf{x}'_1) \phi_i^*(\mathbf{x}_1)$$

$\phi_i(\mathbf{x})$ is the natural spin-orbital with the corresponding occupation number n_i

$$E[N, \Gamma] \Rightarrow E[N, \{n_i, \phi_i\}] = \sum_i n_i H_{ii} + V_{ee}[N, \{n_i, \phi_i\}]$$

N-representability of RDMs

N-representability

RDMs are derivable from an N -particle wave function Ψ_N

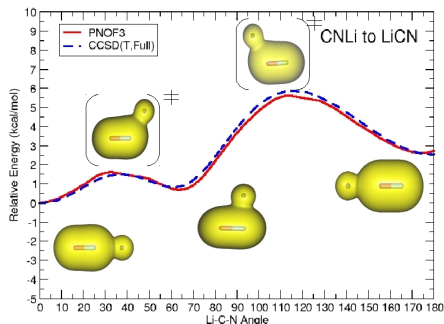
- necessary and sufficient conditions for N-representability of Γ :
Coleman, 1963 $0 \leq n_i \leq 1$ ($\sum_i \Gamma_{ii} = N$)
- lack of sufficient conditions for N-representability of \mathbf{D}

Corollary

Any approximation for $V_{ee}[N, \{n_i, \phi_i\}]$ by $\mathbf{D}[\Gamma]$ must comply at least with the known necessary conditions for the N-representability of the 2-RDM:

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

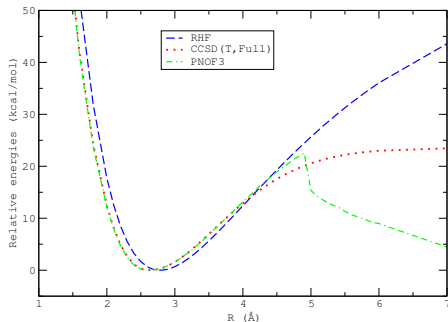
Potential Energy Surface as a function of the LiCN angle



	\angle Li-C-N	PNOF3	CCSD(T, Full)
MIN1	0.0	0.0	0.0
TS	34.5	1.6	1.5
MIN2	58.8	0.7	0.8
TS2	117.8	5.6	5.8
MIN3	180.0	2.5	2.5

- Two step process. Three close-in-energy isomers. Very small barriers: 1.5 kcal/mol and 5.8 kcal/mol.
- The performance of PNOF3 is outstanding. Differences lie within 0.2 kcal/mol.

Dissociation curves of the Li_2 (cc-pVTZ)



- weak covalent bond
- homolytic dissociation
- correct behavior in the equilibrium region
- unphysical lowering at the dissociation limit. Why?

PNOF3 satisfies D and Q conditions, but it fails at the G condition!

$$g^{max}(2.61 \text{ \AA}) = -0.021 \quad g^{max}(7.0 \text{ \AA}) = -0.741$$

Spin Components of RDMs

- $[\widehat{S}_z, \widehat{\mathcal{H}}] = 0; [\widehat{S}^2, \widehat{\mathcal{H}}] = 0 \Rightarrow$ eigenstate $|SM_S\rangle$
- $|\phi_i\rangle = |\varphi_p\rangle \otimes |\sigma\rangle \Rightarrow \left\{ \phi_i(\mathbf{x}) : \varphi_p^\alpha(\mathbf{r})\alpha(\mathbf{s}), \varphi_p^\beta(\mathbf{r})\beta(\mathbf{s}) \right\}$
- The spin contamination effects can straightforwardly be avoided by the use of a single set of orbitals $\{\varphi_p(\mathbf{r})\}$

$$\varphi_p^\alpha(\mathbf{r}) = \varphi_p^\beta(\mathbf{r}) = \varphi_p(\mathbf{r})$$

Independent spin components

$$\Gamma : \Gamma_{pr}^{\alpha\alpha}, \Gamma_{pr}^{\beta\beta} \quad \mathbf{D} : D_{pq,rt}^{\alpha\alpha,\alpha\alpha}, D_{pq,rt}^{\alpha\beta,\alpha\beta}, D_{pq,rt}^{\beta\beta,\beta\beta}$$

Expectation values

$$\textcircled{1} \quad \langle \widehat{S}_z \rangle \equiv M_S = \frac{1}{2} \sum_p \left(n_p^\alpha - n_p^\beta \right) = \frac{N^\alpha - N^\beta}{2}$$

$$\textcircled{2} \quad \langle \widehat{S}^2 \rangle \equiv S(S+1) = -\frac{N(N-4)}{4} \\ + \sum_{pq} \left(D_{pq,pq}^{\alpha\alpha,\alpha\alpha} + D_{pq,pq}^{\beta\beta,\beta\beta} - 2D_{pq,qp}^{\alpha\beta,\alpha\beta} \right)$$

$$\textcircled{3} \quad E = \sum_p \left(n_p^\alpha + n_p^\beta \right) H_{pp} + \sum_{pqrt} \widetilde{D}_{pq,rt} \langle rt|pq \rangle$$

$$\widetilde{D}_{pq,rt} = D_{pq,rt}^{\alpha\alpha,\alpha\alpha} + D_{pq,rt}^{\alpha\beta,\alpha\beta} + D_{pq,rt}^{\beta\alpha,\beta\alpha} + D_{pq,rt}^{\beta\beta,\beta\beta} \quad (\text{spinless})$$

Cumulant expansion of the 2-RDM

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

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

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

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

Δ : real symmetric matrix ($\Delta_{pq}^{\sigma_1\sigma_2} = \Delta_{qp}^{\sigma_2\sigma_1}$)

$$\text{Sum Rules: } \sum_q' \Delta_{pq}^{\sigma\sigma} = n_p^\sigma (1 - n_p^\sigma), \quad \sum_q \Delta_{pq}^{\alpha\beta} = \Pi_{pp}$$

Π : spin-independent Hermitian matrix

$$(\Pi_{pr}^{\alpha\alpha} = \Pi_{pr}^{\beta\beta} = \Pi_{pr}^{\alpha\beta} = \Pi_{pr}^{\beta\alpha} = \Pi_{pr}, \quad \Pi_{pr} = \Pi_{rp}^*)$$

Energy Expression (JKL-functional)

The approximate cumulant leads to the NOF: $(\Delta[\mathbf{n}], \Pi[\mathbf{n}])$

$$E = \sum_p (n_p^\alpha + n_p^\beta) H_{pp} + \frac{1}{2} \sum_{pq} \left[(n_q^\alpha + n_q^\beta) (n_p^\alpha + n_p^\beta) - \tilde{\Delta}_{pq} \right] J_{pq} \\ - \frac{1}{2} \sum_{pq} \left[(n_q^\alpha n_p^\alpha + n_q^\beta n_p^\beta) - (\Delta_{pq}^{\alpha\alpha} + \Delta_{pq}^{\beta\beta}) \right] K_{pq} + \sum_{pr} \Pi_{pr} L_{rp}$$

$$\tilde{\Delta}_{pq} = \Delta_{pq}^{\alpha\alpha} + \Delta_{pq}^{\alpha\beta} + \Delta_{pq}^{\beta\alpha} + \Delta_{pq}^{\beta\beta} \text{ (spinless)}$$

$J_{pq} = \langle pq|pq \rangle$: Coulomb integrals

$K_{pq} = \langle pq|qp \rangle$: exchange integrals

The exchange and time-inversion integral

L_{rp} arises from the correlation between particles with opposite spins:

$$L_{rp} = \int d\mathbf{x}_1 d\mathbf{x}_2 [\varphi_r^\alpha(\mathbf{r}_1) \alpha(\mathbf{s}_1)]^* [\varphi_r^\beta(\mathbf{r}_2) \beta(\mathbf{s}_2)]^* r_{12}^{-1} \varphi_p^\alpha(\mathbf{r}_1) \alpha(\mathbf{s}_1) \varphi_p^\beta(\mathbf{r}_2) \beta(\mathbf{s}_2)$$

or equivalently, $L_{rp} =$

$$\int d\mathbf{x}_1 d\mathbf{x}_2 [\varphi_r^\alpha(\mathbf{r}_1) \alpha(\mathbf{s}_1)]^* [\hat{I} \varphi_p^\alpha(\mathbf{r}_2) \alpha(\mathbf{s}_2)]^* r_{12}^{-1} \hat{I}(2) \hat{P}_{12} \varphi_r^\alpha(\mathbf{r}_1) \alpha(\mathbf{s}_1) \varphi_p^\alpha(\mathbf{r}_2) \alpha(\mathbf{s}_2)$$

where \hat{P}_{12} operator permutes electrons 1 and 2, and the time-inversion antiunitary operator \hat{I} changes a ket vector into bra vector and $\alpha(\beta)$ into $\beta(\alpha)$, i.e.,

$$\hat{I} |p\alpha\rangle = \langle p\beta|, \quad \hat{I} |p\beta\rangle = -\langle p\alpha|$$

real orbitals $\Rightarrow L_{rp} = K_{rp}$

Singlets: $|SM_S\rangle = |00\rangle$

- $\langle \hat{S}^2 \rangle = S(S+1) = 0$, $\langle \hat{S}_z \rangle = \frac{N^\alpha - N^\beta}{2} = 0$
- $n_p^\beta = n_p^\alpha$, $2 \sum_p n_p = N$, $\Delta_{qp}^{\beta\alpha} = \Delta_{qp}^{\alpha\beta}$, $\Delta_{qp}^{\beta\beta} = \Delta_{qp}^{\alpha\alpha}$
- Assume $\Delta_{qp}^{\alpha\alpha} = \Delta_{qp}^{\alpha\beta} = \Delta_{qp}^{\beta\alpha} = \Delta_{qp}^{\beta\beta} = \Delta_{qp}$

$$E^{|00\rangle} = 2 \sum_p n_p H_{pp} + \sum_{pq} (n_q n_p - \Delta_{qp}) (2J_{pq} - K_{pq}) + \sum_{pq} \Pi_{qp} K_{pq}$$

Two-electron NOF for singlets $|SM_S\rangle = |00\rangle$

- $D_{pq,rt}^{\alpha\alpha,\alpha\alpha} = D_{pq,rt}^{\beta\beta,\beta\beta} = 0$
- Full-CI function (Löwdin and Shull 1956, Kutzelnigg 1963):

$$E(2e^-) = 2 \sum_{p=1}^{\infty} n_p H_{pp} + \sum_{p,q=1}^{\infty} \Pi_{qp} K_{pq}$$

$$\Delta_{qp}(2e^-) = n_q n_p,$$

q	p	$\Pi_{qp}(2e^-)$
1	$(1, \infty)$	$-\sqrt{n_q n_p}$
$(1, \infty)$	1	$-\sqrt{n_q n_p}$
$[1, \infty)$	$[1, \infty)$	$\sqrt{n_q n_p}$

for any $2e^-$ system our NOF yields the exact total energy!

- $\Delta_{qp}(2e^-)$ violates the sum $\sum_q' \Delta_{qp} = n_p h_p$ for $N > 2$

Conserving rule for \hat{S}^2 and diagonal elements

- Assume $N^\alpha \geq N^\beta$ and high-spin multiplet state $|SM_S\rangle = |SS\rangle$

$$\langle \hat{S}^2 \rangle = S(S+1) + N^\beta - \sum_p n_p^\alpha n_p^\beta - 2 \sum_{pq} \lambda_{pq,qp}^{\alpha\beta,\alpha\beta}$$

conservation of the total spin $\rightarrow 2 \sum_{pq} \lambda_{pq,qp}^{\alpha\beta,\alpha\beta} = N^\beta - \sum_p n_p^\alpha n_p^\beta$

J. Chem. Phys. 131, 021102 (2009).

- $\lambda_{pq,qp}^{\alpha\beta,\alpha\beta} = \frac{1}{2} (\Pi_{pp} - \Delta_{pp}^{\alpha\beta}) \delta_{pq}$ for our reconstruction
 $n_p^\alpha = n_p + m_p, n_p^\beta = n_p$

spin conserving rule:

$$\Delta_{pp}^{\alpha\beta} = n_p^\alpha n_p^\beta = n_p^2 + n_p m_p, \quad \Pi_{pp} = n_p$$

The N-representability and off-diagonal elements

- Δ : real symmetric matrix ($\Delta_{pq}^{\sigma\sigma'} = \Delta_{q'p}^{\sigma'\sigma}$)
- Π : spin-independent Hermitian matrix ($\Pi_{pr} = \Pi_{rp}^*$)
- Sum Rules: $\sum_q' \Delta_{pq}^{\sigma\sigma} = n_p^\sigma h_p^\sigma$, $\sum_q \Delta_{pq}^{\alpha\beta} = \Pi_{pp}$

One may approximate the unknown $\Delta[\mathbf{n}]$ and $\Pi[\mathbf{n}]$, in terms of the occupation numbers, considering the analytic constraints imposed by necessary N-representability conditions.

- $D \geq 0, Q \geq 0 \Rightarrow \Delta_{qp}^{\sigma\sigma'} \leq n_q^\sigma n_p^{\sigma'}, \Delta_{qp}^{\sigma\sigma'} \leq h_q^\sigma h_p^{\sigma'}, q \neq p$
- $G \geq 0 \Rightarrow \Pi_{qp}^2 \leq n_q h_q n_p h_p + \Delta_{qp}^{\alpha\beta} (n_q h_p + h_q n_p) + [\Delta_{qp}^{\alpha\beta}]^2$

Implemented Approximations

- PNOF1
Int. J. Quan. Chem. 106, 1093, 2006.
- PNOF2
J. Chem. Phys. 126, 214103, 2007.
- PNOF3
J. Chem. Phys. 132, 031103, 2010.
- PNOF4
J. Chem. Phys. 133, 111101, 2010.
- PNOF5
J. Chem. Phys. 134, 164102, 2011.



(J. Comp. Chem. 30, 2078, 2009)

strengths and weaknesses of the different PNOFs are assessed in
Review Article: Int. J. Quantum Chem. DOI: 10.1002/qua.24020

PNOF5: Δ - and Π -matrices for singlet states $|S = 0\rangle$

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

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

$$E^{PNOF5} = 2 \sum_{p=1}^N n_p H_{pp} + \sum_{p,q=1}'' n_q n_p (2J_{pq} - K_{pq}) \\ + \sum_{p=1}^N (n_p J_{pp} - \sqrt{n_{\tilde{p}}n_p} K_{p\tilde{p}})$$

$$(\tilde{p} = N - p + 1; \quad \sum'' : q \neq p, \tilde{p})$$

Minimization of the functional E^{PNOF5} under constraints

- 1 Löwdin's normalization: $2 \sum_p n_p = N$ ($n_{\bar{p}} + n_p = 1$)
- 2 N representability of the 1-RDM: $0 \leq n_p \leq 1$
 $\implies n_p = \cos^2 \gamma_p, n_{\bar{p}} = \sin^2 \gamma_{\bar{p}}$: Conjugate Gradient Method

- 3 Orthonormality of natural orbitals: $\langle \varphi_p | \varphi_q \rangle = \delta_{pq}$

\implies Method of Lagrangian multipliers

$$\Omega = E - 2 \sum_{pq} \varepsilon_{qp} [\langle \varphi_p | \varphi_q \rangle - \delta_{pq}]$$

Euler equations for the natural orbitals $\{\varphi_p(\mathbf{r})\}$

$$n_p \hat{V}_p |\varphi_p\rangle = \sum_q \varepsilon_{qp} |\varphi_q\rangle, \quad \varepsilon_{qp} = n_p \langle \varphi_q | \hat{V}_p | \varphi_p \rangle$$

$$\hat{V}_p(1) = \hat{H}(1) + \hat{J}_p(1) - \sqrt{\frac{n_p}{n_p}} \hat{K}_p(1) + \sum_{q=1}^N n_q \left[2\hat{J}_q(1) - \hat{K}_q(1) \right]$$

$[\Lambda, \Gamma] \neq 0 \Rightarrow$ solution cannot be reduced to diagonalization of Λ

$$\Lambda = \{\varepsilon_{qp}\}, \quad \Gamma = \{n_p \delta_{pq}\}$$

- Self-consistent iterative diagonalization procedure

J. Comp. Chem. 30, 2078 (2009)

The Hermiticity of Λ and the Aufbau Principle

- The Lagrangian is Hermitian at the extremum: $\varepsilon_{pq} = \varepsilon_{qp}^*$
 - Define a new Hermitian matrix **F**: (off-diagonal elements)

$$F_{pq} = \theta(q - p) [\varepsilon_{pq} - \varepsilon_{qp}^*] + \theta(p - q) [\varepsilon_{qp}^* - \varepsilon_{pq}]$$

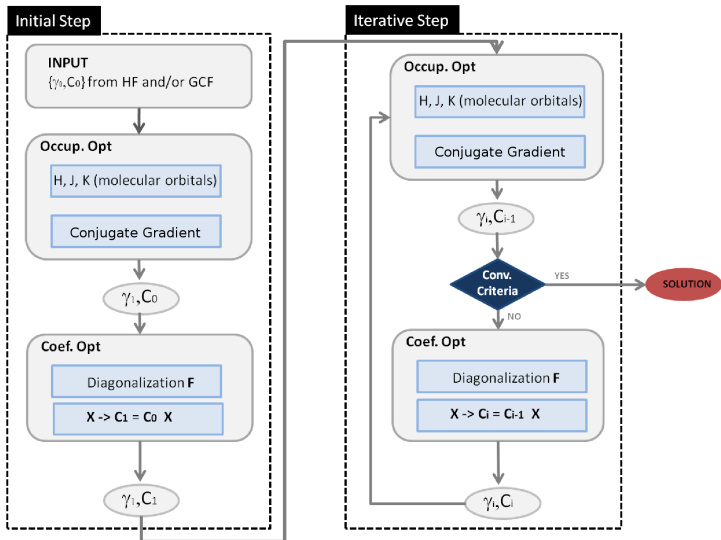
- $\{F_{pp}\}$ cannot be determined from the Hermiticity of Λ
- First order perturbative theory (Hillier 1970, Saunders 1973)

$$E = E^0 + 2 \sum_{p < q} \Delta_{pq} F_{pq}^0 = E^0 + 2 \sum_{p < q} \frac{|F_{pq}^0|^2}{F_{pp}^0 - F_{qq}^0}$$

$\{F_{qq}^0 > F_{pp}^0\} \rightarrow E$ is bound to drop upon diagonalization of **F**⁰

\Rightarrow Aufbau Principle for diagonal elements

J. Comp. Chem. 30, 2078 (2009)



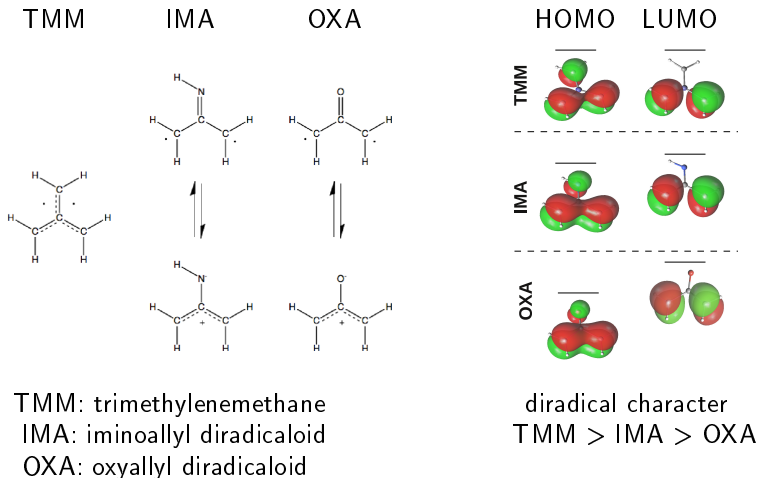
Parallel Efficiency (H₂O, cc-pV6Z, 290 GBF)

cores (n)	nodes	Time (h)	Total # Iter.	$E_n = \frac{T_1}{nT_n} \frac{IT_n}{IT_1} \times 100\%$
1	1	62.6	998	100
2	1	34.5	1090	99
4	2	16.2	1004	97
8	2	8.1	1013	98
12	3	5.8	1056	95
24	2	2.5	866	91
24	4	2.5	866	90
36	3	1.9	945	87
48	4	1.7	1115	86

Maximum speedup that can be achieved is $1/(1-P) \sim 40$
 P is the proportion of the program made parallel ($\sim 97.5\%$)

the method scales as $N^4!$ (N : number of orbitals)

Planar trimethylenemethane



Relative Energies and Occupation Numbers

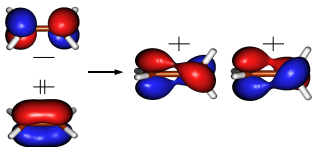
Relative energy with respect to its cyclic isomer, in kcal/mol

	TMM	IMA	OXA
CAS(12,12)	34.4	34.0	26.2
PNOF5	40.8	37.2	26.5
CASPT2(12,12)	43.3	39.7	32.6

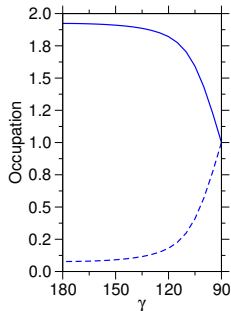
Occupation numbers of the (pseudo)degenerate orbitals

	TMM	IMA	OXA
PNOF4	1.07/0.97	1.36/0.71	1.57/0.50
PNOF5	1.00/1.00	1.26/0.74	1.46/0.54
CAS(12,12)	1.01/0.99	1.25/0.75	1.45/0.55

Ethylene Torsion



Natural Orbital Functional Theory correctly describes degeneracy effects in diradical reactions



J. Chem. Phys. 134, 164102, 2011

Ethylene Torsion. Energetics

	E (Hartrees)		ΔE (kcal/mol)
	Min(D_{2h}) [†]	TS (D_{2d}) [†]	
CASPT2(12,12)	-78.342567	-78.238122	65.5
PNOF5	-78.136524	-78.032063	65.6
B3LYP [‡]	-78.591976	-78.490308	63.8
PBE0 [‡]	-78.485589	-78.388529	60.9
M06-2X [‡]	-78.543689	-78.437072	66.9

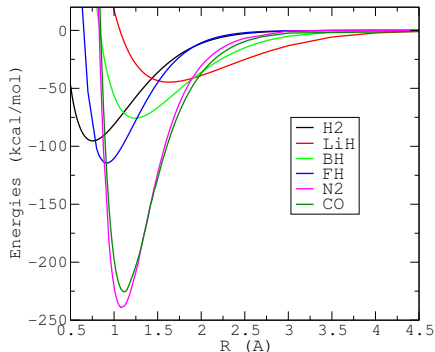
[‡] cc-pVDZ Basis Set.

[†] Optimized at the CASSCF(4,4)/cc-pVDZ level of theory.

[‡] Broken symmetry energies for TS. $\langle S^2 \rangle = 1.01$

J. Chem. Phys. 134, 164102, 2011

cc-pVTZ dissociation curves

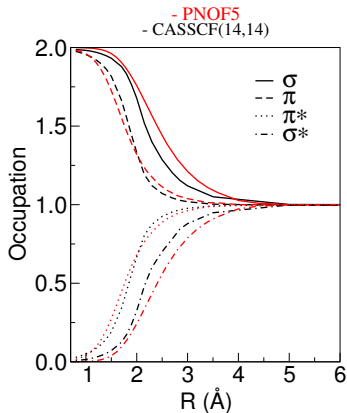
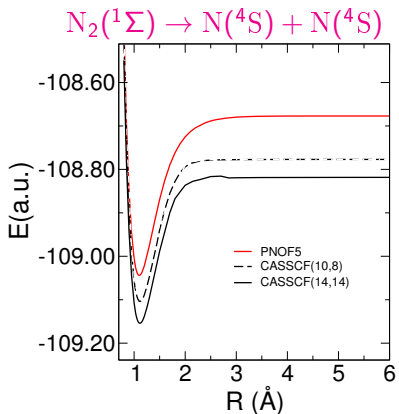


BONDS

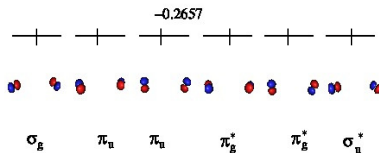
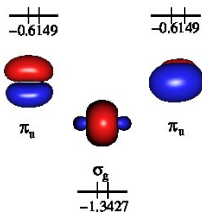
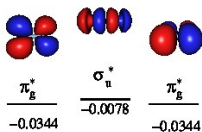
- covalent with different polarity H_2 , FH , BH
- multiple bond CO , N_2
- electrostatic LiH

In all cases, dissociation limit implies an homolytic cleavage of the bond, high degree of near-degeneracy at the dissociation asymptote

J. Chem. Phys. 134, 164102, 2011; J. Chem. Theory Comput. 8, 2646 (2012).

Dissociation for multiply bonded molecule: N_2 

Phys. Chem. Chem. Phys. 13, 20129, 2011

Valence natural orbitals of N₂

cc-pVTZ Ionization Potentials of N₂, in eV

EKT: diagonalization of the matrix ν whose elements are

$$\nu_{qp} = -\frac{\epsilon_{qp}}{\sqrt{n_q n_p}}$$

Molecule	MO	KT	PNOF5-EKT	EXP
N ₂	σ_g	17.23 (1.63)	16.69 (1.09)	15.60
	π_u	16.68 (0.00)	17.50 (0.82)	16.68
	σ_u	21.18 (2.40)	20.45 (1.67)	18.78

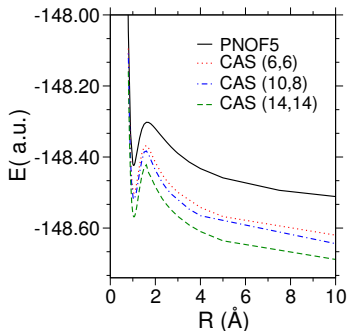
J. Chem. Phys. 136, 174116 (2012)

14-electron isoelectronic series

	N ₂					CN ⁻				
	R _e	D _e	BO	μ _e	q _N	R _e	D _e	BO	μ _e	q _N
PNOF5	1.099	229.9	2.87	0.000	7	1.180	247.6	2.89	0.900	7
CAS(10,8)	1.117	205.0	2.85	0.000	7	1.200	220.0	2.86	2.241	7
CAS(14,14)	1.115	210.4	2.85	0.000	7	1.196	235.4	2.86	2.360	7
Exptl.	1.098	225.1	-	0.000	7	1.177	-	-	0.630	7
	NO ⁺					CO				
	R _e	D _e	BO	μ _e	q _N	R _e	D _e	BO	μ _e	q _C
PNOF5	1.059	228.2	2.87	0.337	6/7	1.130	221.0	2.92	0.209	6
CAS(10,8)	1.077	229.0	2.84	2.368	7	1.143	249.9	2.88	-0.259	6
CAS(14,14)	1.076	261.7	2.83	2.260	6	1.145	247.0	2.86	-0.059	6
Exptl.	1.066	-	-	-	7	1.128	256.2	-	0.112	6

R_e in Å, D_e in kcal/mol and μ_e in Debyes

Phys. Chem. Chem. Phys. 13, 20129, 2011

Dissociation curves for O_2^{2+} 

	R_e (Å)	BO	R^\ddagger (Å)	ΔE^\ddagger ($\frac{kcal}{mol}$)	D_e ($\frac{kcal}{mol}$)	qO
PNOF5	1.038	2.78	1.66	76.5	-71.5	7
(6,6)	1.051	2.79	1.59	83.9	-90.9	7
(10,8)	1.054	2.79	1.59	85.5	-94.8	7
(14,14)	1.052	2.79	1.59	91.9	-92.0	7
MRCI†	1.050	-	1.59	63.3	-	7

† R. H. Nobes, et. al. *Chem. Phys. Lett.* 182, 216 (1991)

Phys. Chem. Chem. Phys. 13, 20129, 2011

Canonical Orbitals

$$E = \sum_{p=1}^N [n_p H_{pp} + \varepsilon_{pp}], \quad \varepsilon_{pp} = n_p \langle \varphi_p | \hat{V}_p | \varphi_p \rangle$$

- the trace of square matrix is the sum of its diagonal elements,

$$E = \text{Tr}(\mathbf{H}\mathbf{\Gamma} + \mathbf{\Lambda}), \quad \mathbf{\Lambda} = \{\varepsilon_{qp}\}$$

- the trace of a matrix is invariant under \mathbf{U} ($\mathbf{X}' = \mathbf{U}^\dagger \mathbf{X} \mathbf{U}$)

$$\text{Tr}(\mathbf{H}\mathbf{\Gamma} + \mathbf{\Lambda}) = \text{Tr}(\mathbf{H}'\mathbf{\Gamma}' + \mathbf{\Lambda}'),$$

$$\square \mathbf{U} : \mathbf{\Lambda}' = \mathbf{U}^\dagger \mathbf{\Lambda} \mathbf{U} \Rightarrow \varepsilon'_{qp} = \varepsilon_p \delta_{qp}, \quad \mathbf{\Gamma}' = \mathbf{U}^\dagger \mathbf{\Gamma} \mathbf{U} \Rightarrow n'_{qp} \neq n_p \delta_{qp}$$

$\{\chi_p(\mathbf{r})\}$: canonical orbitals

Molecular orbital representations

Natural Orbitals $\{\varphi_p(\mathbf{r})\}$

$$\Omega = E - 2 \sum_{pq} \varepsilon_{qp} [\langle \varphi_p | \varphi_q \rangle - \delta_{pq}]$$

Euler Eqs.:

$$n_p \hat{V}_p |\varphi_p\rangle = \sum_q \varepsilon_{qp} |\varphi_q\rangle$$

$$\varepsilon_{qp} = n_p \langle \varphi_q | \hat{V}_p | \varphi_p \rangle$$

$$\Lambda = \{\varepsilon_{qp}\}, \quad \Gamma = \{n_p \delta_{pq}\}$$

$[\Lambda, \Gamma] \neq 0 \Rightarrow$ solution cannot be reduced
 to diagonalization of Λ

*Self-consistent iterative diagonalization
 procedure: JCC 30, 2078 (2009)*

Canonical Orbitals $\{\chi_p(\mathbf{r})\}$

$$E = \sum_p [n_p H_{pp} + \varepsilon_{pp}]$$

$$\varepsilon_{pp} = n_p \langle \varphi_p | \hat{V}_p | \varphi_p \rangle \neq \text{IPs}$$

$$\text{EKT: } \nu_{qp} = -\frac{\varepsilon_{qp}}{\sqrt{n_q n_p}}$$

$$E = \text{Tr}(\mathbf{H}\mathbf{\Gamma} + \mathbf{\Lambda}), \quad \mathbf{\Lambda} = \{\varepsilon_{qp}\}$$

$$U : X' = U^\dagger X U, \quad U^\dagger = U^{-1}$$

$$\text{Tr}(\mathbf{H}\mathbf{\Gamma} + \mathbf{\Lambda}) = \text{Tr}(\mathbf{H}'\mathbf{\Gamma}' + \mathbf{\Lambda}')$$

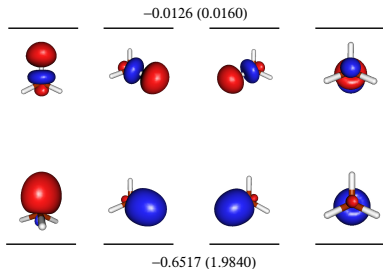
$$\square \Lambda' = U^\dagger \Lambda U, \quad \Gamma' = U^\dagger \Gamma U$$

$$\Lambda' = \{\varepsilon'_p \delta_{qp}\}, \quad \Gamma' = \{n'_p\}$$

$$\Rightarrow \Lambda' |\chi_p\rangle = \varepsilon'_p |\chi_p\rangle$$

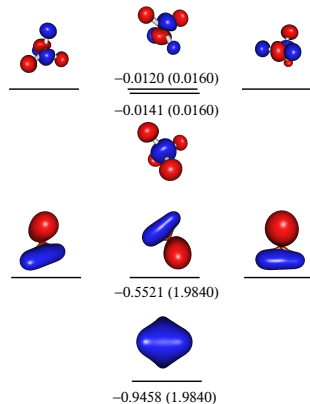
Valence orbitals of methane (CH_4)

Natural Orbital Representation



E

Canonical Orbital Representation



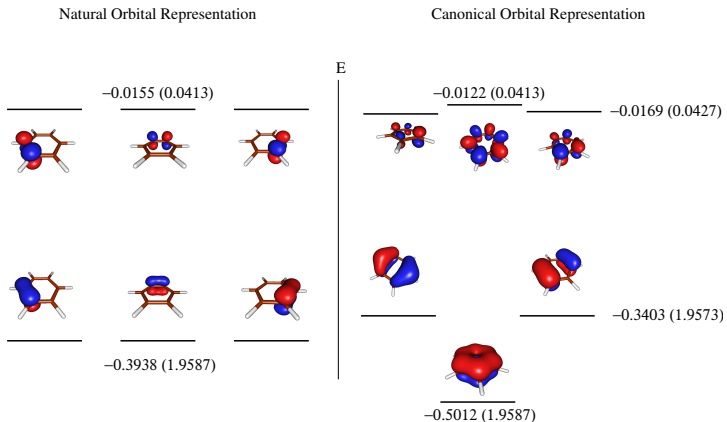
Valence vertical ionization energies, in eV, for methane

	cc-pVDZ	
	T ₂	A ₁
B3LYP	10.57	18.79
BLYP	9.13	16.66
BP86	9.33	16.93
M06-2X	12.22	21.20
M06L	9.56	17.76
M06	10.74	18.98
MPWPW91	9.27	16.87
O3LYP	9.98	18.06
Experiment	14.40	23.00

	cc-pVDZ	
	T ₂	A ₁
OLYP	9.17	16.88
PBEPBE	9.22	16.83
PBEHPBE	9.23	16.82
PW91PW91	9.29	16.88
HF	14.76	25.62
$-\epsilon_{pp}^{CanOrb}$	15.02	25.74
EKT-PNOF5	15.14	25.89
OVGF	14.21	23.47
Experiment	14.40	23.00

Chem. Phys. Lett. 531, 272, 2012.

Valence orbitals of Benzene (C_6H_6)



ChemPhysChem 13, 2297, 2012, Theor. Chem. Acc. 2013

Announcement

- Dr. Jon M. Matxain

“Natural Orbital Functional Theory Applied to Biologically relevant systems: Oxydative Stress in Amino Acid Side Chains”

January 17, 12:00, Sala de Graus

- Dr. Fernando Ruipérez

“Structure and bonding in transition metal containing systems: natural orbital functional and wavefunction-based calculations”

January 17, 12:30, Sala de Graus

Closing Remarks

- it is now feasible to perform expensive NOFT calculations. The parallelization of the bottlenecks of our code allows us to achieve an execution ~ 40 times faster than the sequential one.
- the functional N-representability plays a crucial role towards achieving chemical accuracy.
- The PNOF5 can describe in a balanced way chemical bonding situations that evolve gradually from non-degenerate to degenerate states. Integer number of electrons have been found on the dissociated atoms.
- two equivalent orbital representations are possible. PNOF5 could be a practical tool for the interpretation of the chemical bonding.

Acknowledgement

- Financial support comes from the Basque Government and the Spanish Office for Scientific Research.
- The SGI/IZO-SGIker UPV/EHU is greatly acknowledged for generous allocation of computational resources.

Thank you for your attention !!!