

# The Molecular Orbitals in NOFT

Workshop on ab initio valence bond theory

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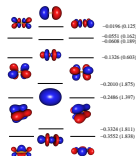
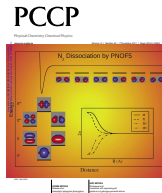
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# Outline

- 1 Introduction to the NOFT
- 2 PNOF5 Results
  - examples of systems, where DFT yields pathological failures
  - potentiality of the NOF theory.
- 3 PNOF5 Molecular Orbitals



# The electronic energy $E$ for $N$ -electron systems

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

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

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

# 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  $\Gamma$

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

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  $n_i$ ;

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

Ansatz for singlet states  $|S = 0\rangle$ 

Int. J. Quantum Chem. 106, 1093 (2006)

- Spin-blocks of the 2-RDM:

$$D_{pq,rt}^{\sigma\sigma,\sigma\sigma} = \frac{1}{2} (n_p n_q - \Delta_{pq}) (\delta_{pr} \delta_{qt} - \delta_{pt} \delta_{qr}) \quad (\sigma = \alpha, \beta)$$

$$D_{pq,rt}^{\alpha\beta,\alpha\beta} = \frac{1}{2} (n_p n_q - \Delta_{pq}) \delta_{pr} \delta_{qt} + \frac{\Pi_{pr}}{2} \delta_{pq} \delta_{rt}$$

$\Delta \{n_p\}, \Pi \{n_p\}$  : real symmetric matrices

$$\text{Sum Rule: } \sum_q' \Delta_{pq} = n_p (1 - n_p)$$

- Conserving rule for  $\hat{S}^2 \Rightarrow$  diagonal elements
- N-representability  $\Rightarrow$  inequalities for off-diagonal elements

PNOF5:  $\Delta$ - and  $\Pi$ -matrices for singlet states  $|S = 0\rangle$ 

$$\Delta_{pq} = n_p^2 \delta_{pq} + n_p n_{\tilde{p}} \delta_{\tilde{p}q}$$

$$\Pi_{pq} = n_p \delta_{pq} - \sqrt{n_p n_{\tilde{p}}} \delta_{\tilde{p}q}$$

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

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

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

# Minimization of the functional $E[N, \{\varphi_p\}]$

Constraints:

① Löwdin's normalization:  $2 \sum_p n_p = N \quad (n_{\bar{p}} + n_p = 1)$

②  $N$  representability of the 1-RDM:  $0 \leq n_p \leq 1$

$\implies n_p = \cos^2 \gamma_p, n_{\bar{p}} = \sin^2 \gamma_{\bar{p}} : \text{Conjugate Gradient Method}$

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

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

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

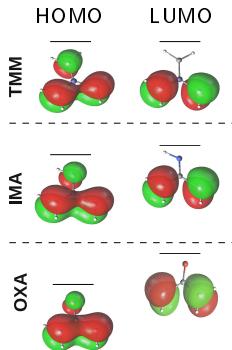
$[\Lambda, \Gamma] \neq 0 \Rightarrow$  solution cannot be reduced to diagonalization of  $\Lambda$

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

- Self-consistent iterative diagonalization procedure

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

## Planar trimethylenemethane



Relative energy to its cyclic isomer (kcal/mol)

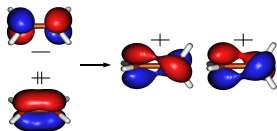
	TMM	IMA	OXA
CAS(12,12)	34.4	34.0	26.2
<b>PNOF5</b>	<b>40.8</b>	<b>37.2</b>	<b>26.5</b>
CASPT2(12,12)	43.3	39.7	32.6

Occupation numbers of (quasi)degenerate orbitals

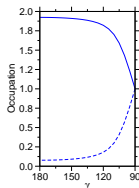
	TMM	IMA	OXA
PNOF4	1.07/0.97	1.36/0.71	1.57/0.50
<b>PNOF5</b>	<b>1.00/1.00</b>	<b>1.26/0.74</b>	<b>1.46/0.54</b>
CAS(12,12)	1.01/0.99	1.25/0.75	1.45/0.55

## Ethylene Torsion

J. Chem. Phys 134, 164102, 2011



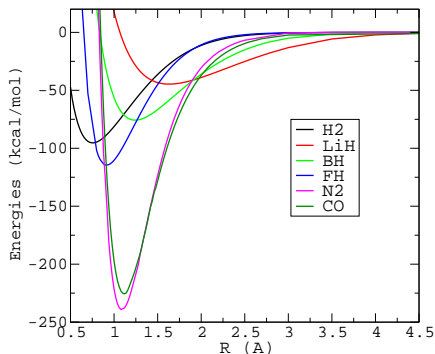
Natural Orbital Functional Theory correctly describes degeneracy effects in diradical reactions



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

<sup>†</sup> cc-pVDZ Basis Set, <sup>‡</sup> Broken symmetry energies for TS.  $\langle \hat{S}^2 \rangle = 1.01$

# cc-pVTZ dissociation curves for diatomic molecules



## 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

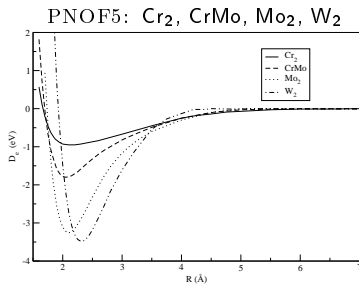
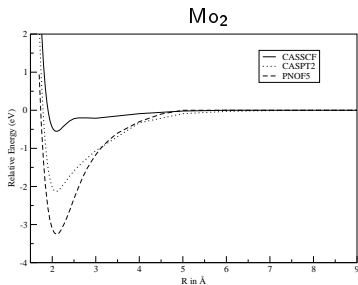
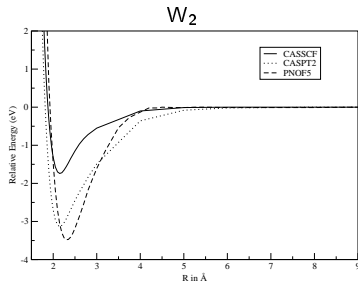
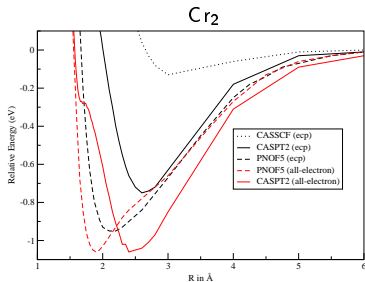
## Homolytic Dissociations: 14-electron isoelectronic series

	$N_2$					$CN^-$				
	$R_e$	$D_e$	BO	$\mu_e$	$q_N$	$R_e$	$D_e$	BO	$\mu_e$	$q_N$
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	$\mu_e$	$q_N$	$R_e$	$D_e$	BO	$\mu_e$	$q_C$
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  $\mu_e$  in Debyes

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

# Dissociation of transition metal dimers (ECP, 6s5p3d)



# Molecular orbital representations

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

Orthonormality:  $\langle \varphi_p | \varphi_q \rangle = \delta_{pq}$

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

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  $\Lambda$

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

## Molecular orbital representations

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

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

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

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

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

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

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

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

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

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

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

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

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

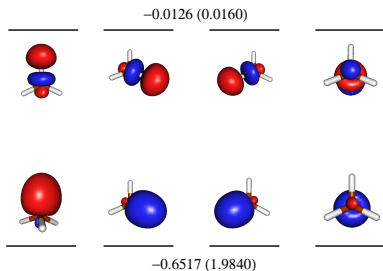
$$\mathbf{\Lambda}' = \{\varepsilon'_p \delta_{qp}\}, \quad \mathbf{\Gamma}' = \{n'_{qp}\}$$

$$\Rightarrow \mathbf{\Lambda}' |\chi_p\rangle = \varepsilon'_p |\chi_p\rangle$$

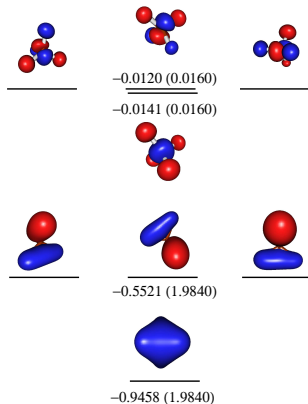


# PNOF5 valence orbitals of methane ( $CH_4$ )

Natural Orbital Representation



Canonical Orbital Representation



ChemPhysChem 13, 2297, 2012, Phys. Chem. Chem. Phys. 2012

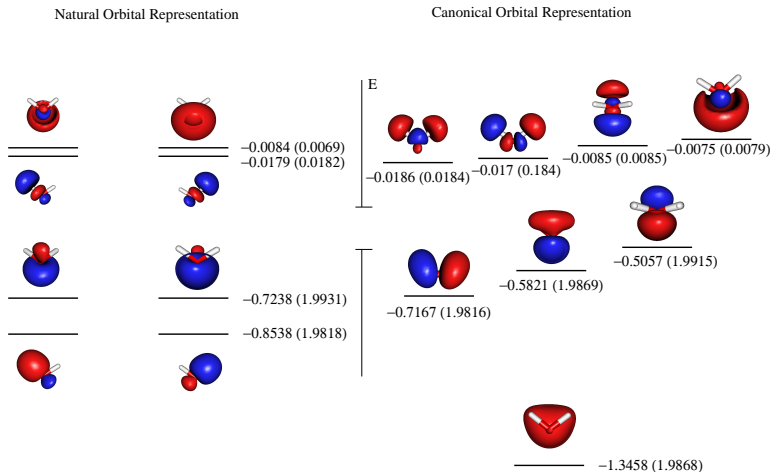
## Valence vertical ionization energies, in eV, for methane

	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
$-\varepsilon_{pp}^{CanOrb}$	15.02	25.74
EKT-PNOF5	15.14	25.89
OVSF	14.21	23.47
Experiment	14.40	23.00

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

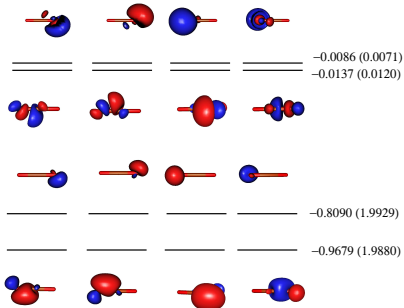
# PNOF5 valence orbitals of water ( $H_2O$ )



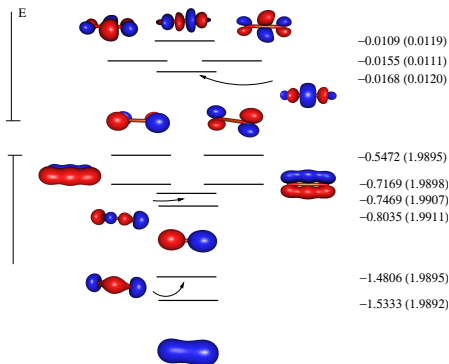
ChemPhysChem 13, 2297, 2012, Phys. Chem. Chem. Phys. 2012

# Valence orbitals of carbon dioxide ( $\text{CO}_2$ ). Banana Orbitals.

Natural Orbital Representation

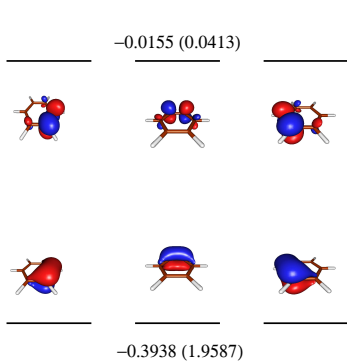


Canonical Orbital Representation

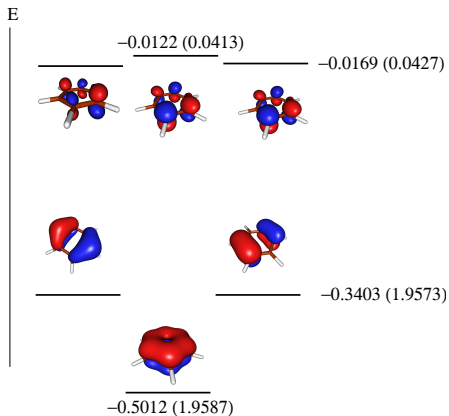


# Aromaticity: PNOF5 valence orbitals of benzene ( $C_6H_6$ )

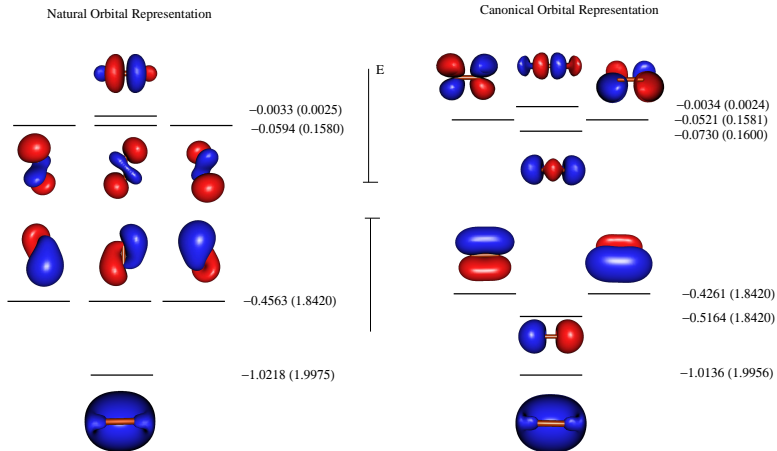
Natural Orbital Representation



Canonical Orbital Representation

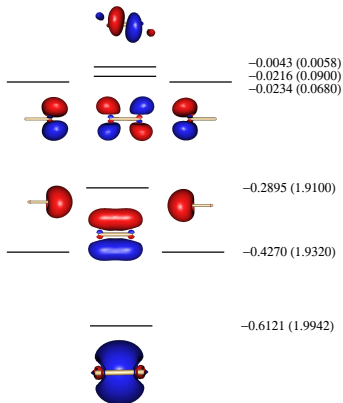


# Valence orbitals of carbon dimer ( $C_2$ )

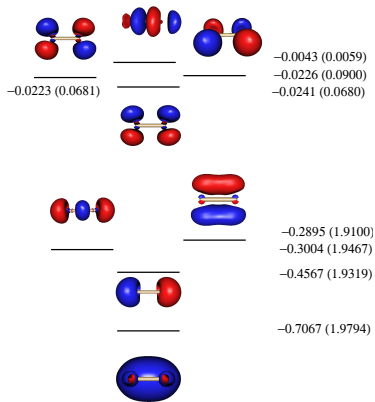


# Valence orbitals of silicon dimer ( $Si_2$ )

Natural Orbital Representation



Canonical Orbital Representation



## Closing Remarks

- Two orbital pictures are possible: NOs and COs.
- The COs can be obtained only after solving the problem in the NO representation.
- PNOF5 NOs are localized orbitals that nicely agree with the chemical intuition of chemical bonding, VB and VSEPR bonding pictures.
- PNOF5 COs are symmetry-adapted delocalized orbitals similar to those obtained by molecular orbital theories.
- NO and CO representations are unique one-particle pictures of the same solution ergo complement each other in the description of the electronic structure.



## Acknowledgement

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- The SGI/IZO-SGIker UPV/EHU is greatly acknowledged for generous allocation of computational resources.

Thank you for your attention !!!