Can NOFT bridge the gap between DFT and WFT?

Kathmandu Workshop on Theoretical Chemistry

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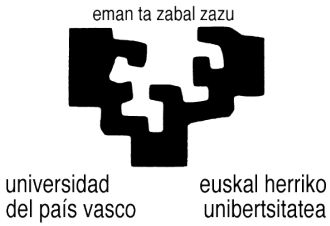
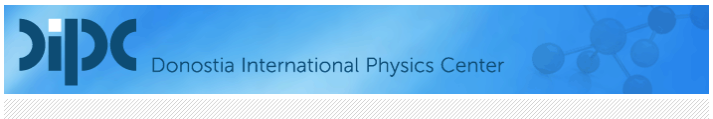




The electronic energy E for N-electron systems

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

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

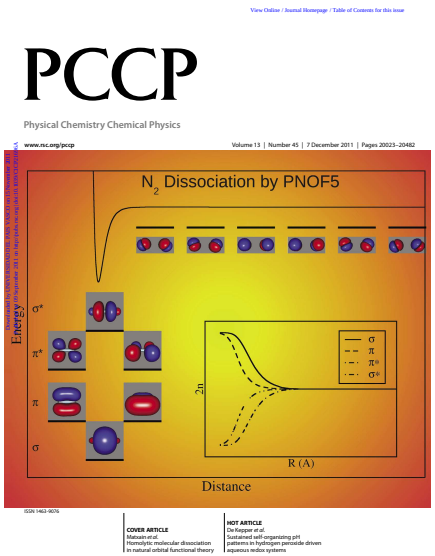
$E[N, \Gamma, \mathbf{D}]$ is an explicitly known functional of the 1- and 2-RDMs!

Variational Methods:

$$DFT \quad \underset{\rho(\mathbf{r}) \Longrightarrow}{(reconstruction)} \quad \underset{\Gamma, D}{RDMs} \quad \underset{\Longleftarrow \Gamma^N \leftarrow \Psi}{(contraction)} \quad CI, MCSCF, CCSD, \ldots$$

Outline

1. Introduction to the DMFT and NOFT
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. Closing Remarks



1-RDM Functional

Last term in the Energy: $U[N,\mathbf{D}] = \sum_{ijkl} < ij|kl > D_{kl,ij}$ 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 $\{\phi_i(\mathbf{x})\}$:

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

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

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

Cumulant expansion of the 2-RDM

$$D^{\sigma\sigma,\sigma\sigma}_{pq,rt} = \frac{n^\sigma_p n^\sigma_q}{2}\left(\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr}\right) + \lambda^{\sigma\sigma,\sigma\sigma}_{pq,rt} \quad (\sigma = \alpha, \beta)$$

$$D^{\alpha\beta,\alpha\beta}_{pq,rt} = \frac{n^\alpha_p n^\beta_q}{2}\delta_{pr}\delta_{qt} + \lambda^{\alpha\beta,\alpha\beta}_{pq,rt}$$

$$\lambda^{\sigma\sigma,\sigma\sigma}_{pq,rt} = -\frac{\Delta^{\sigma\sigma}_{pq}}{2}\left(\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr}\right)$$

$$\lambda^{\alpha\beta,\alpha\beta}_{pq,rt} = -\frac{\Delta^{\alpha\beta}_{pq}}{2}\delta_{pr}\delta_{qt} + \frac{\Pi_{pr}}{2}\delta_{pq}\delta_{rt}$$

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

Sum Rules: $\sum_q{}' \Delta^{\sigma\sigma}_{pq} = n^\sigma_p\left(1 - n^\sigma_p\right)$, $\sum_q \Delta^{\alpha\beta}_{pq} = \Pi_{pp}$

Π : *spin-independent Hermitian matrix*

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

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

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

- Assume $N^\alpha \geq N^\beta$ and high-spin multiplet state $M_S = S$

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

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

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

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

$n_p^\alpha = n_p + m_p\,,\ n_p^\beta = n_p$

spin conserving rule:

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

The N-representability and off-diagonal elements

N-representability

RDMs must be derivable from an N-particle wave function Ψ

- N-representability of Γ: $0 \leq n_i \leq 1 \quad (\sum_i n_i = N)$
- lack of sufficient conditions for N-representability of $\mathbf{D}$

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 of the 2-RDM.

- $D \geq 0, Q \geq 0 \quad \Rightarrow \quad \Delta_{qp}^{\sigma_1\sigma_2} \leq n_q^{\sigma_1} n_p^{\sigma_2}, \ \Delta_{qp}^{\sigma_1\sigma_2} \leq h_q^{\sigma_1} h_p^{\sigma_2}$
- $G \geq 0 \quad \Rightarrow \quad \Pi_{qp}^2 \leq n_q h_q n_p h_p + \Delta_{qp}\left(n_q h_p + h_q n_p\right) + \Delta_{qp}^2$

Implemented Approximations

- PNOF1: Int. J. Quantum 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.

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

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

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

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

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

J. Chem. Phys. 134, 164162, 2011

Minimization of the functional E^{PNOF5} under constraints

1. Löwdin's normalization: $2\sum_p n_p = N \qquad (n_{\tilde{p}} + n_p = 1)$
2. N representability of the 1-RDM: $0 \leq n_p \leq 1$

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

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

$$\Longrightarrow \quad \text{Method of Lagrangian multipliers}$$

$$\Omega = E - 2\sum_{pq} \varepsilon_{qp} \left[< \varphi_p | \varphi_q > - \delta_{pq} \right]$$

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

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

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

$[\Lambda, \Gamma] \neq 0 \Rightarrow$ 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 Hermeticity 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)

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

  - $\{F_{pp}\}$ cannot be determined from the Hermiticity of Λ

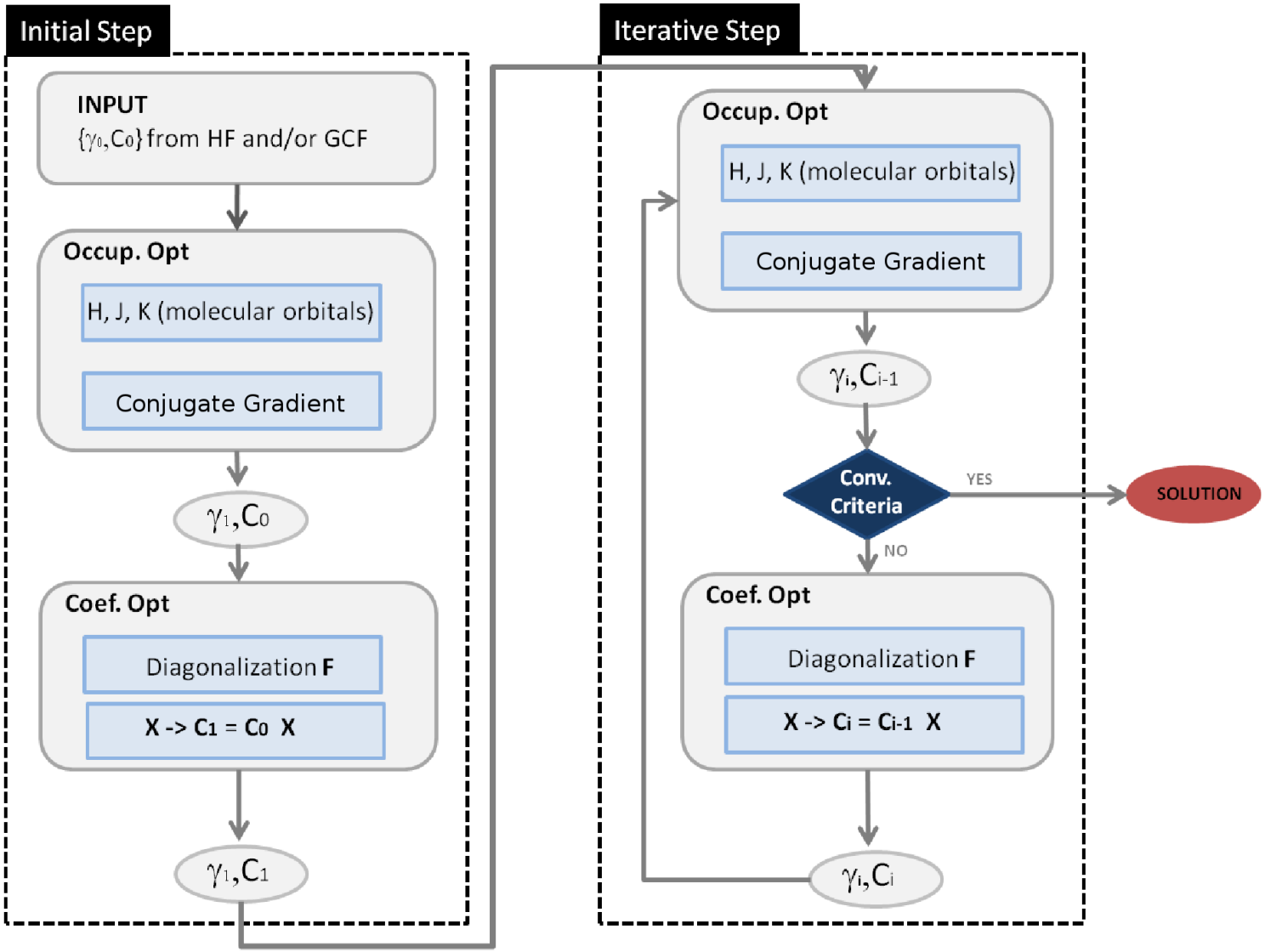
- First order perturbative theory (Hillier 1970, Saunders 1973)

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

$\left\{F^0_{qq} > F^0_{pp}\right\} \rightarrow E$ is bound to drop upon diagonalization of $\mathbf{F^0}$

$\Rightarrow$ Aufbau Principle for diagonal elements

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


Initial Step
INPUT
{γ0,C0} from HF and/or GCF
Occup. Opt
H, J, K (molecular orbitals)
Conjugate Gradient
γ1,C0
Coef. Opt
Diagonalization F
X -> C1 = C0 X
γ1,C1
Iterative Step
Occup. Opt
H, J, K (molecular orbitals)
Conjugate Gradient
γi,Ci-1
Conv. Criteria
YES
SOLUTION
NO
Coef. Opt
Diagonalization F
X -> Ci = Ci-1 X
γi,Ci

Parallel Efficiency (H_2O, cc-pV6Z, 290 GBF)

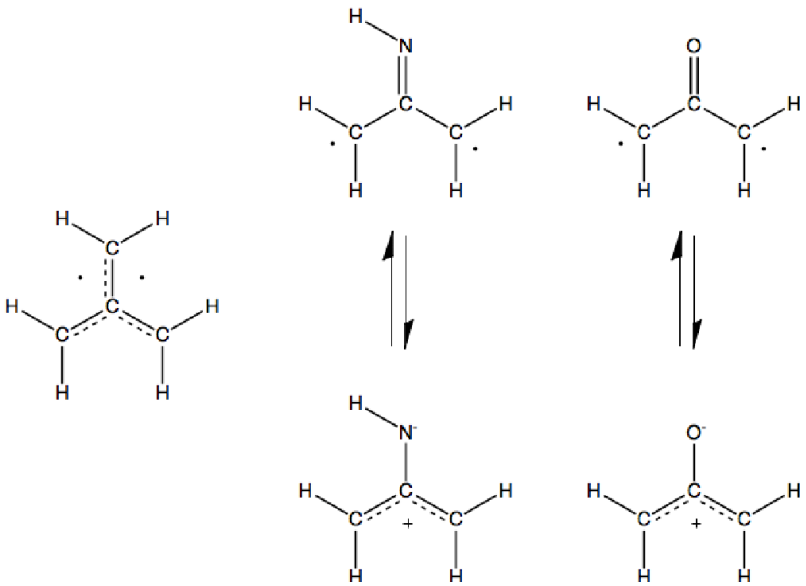
cores (n)	nodes	Time (h)	Total # Iter.	Efficiency (%)
1	1	62.6	998	100
2	1	34.5	1090	99
4	2	16.2	1004	97
8	2	8.1	1013	98
12	3	5.8	1056	95
24	2	2.5	866	91
24	4	2.5	866	90
36	3	1.9	945	87
48	4	1.7	1115	86

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

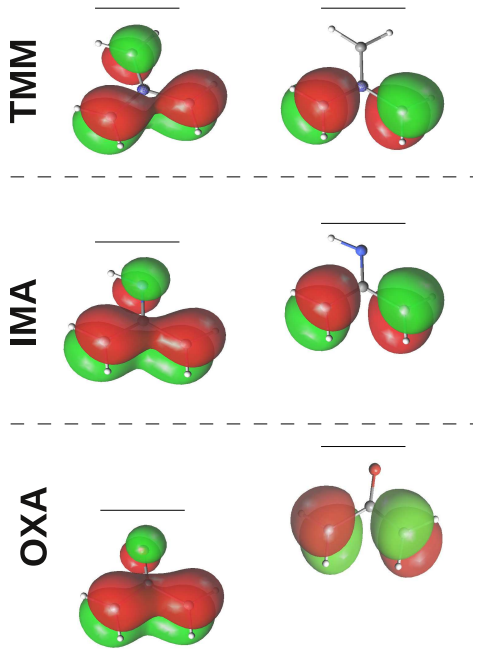
$$E_n = \frac{T_1}{nT_n}\,\frac{IT_n}{IT_1} \times 100\%$$

Planar trimethylenemethane

TMM IMA OXA



HOMO LUMO



TMM: trimethylenemethane
IMA: iminoallyl diradicaloid
OXA: oxyallyl diradicaloid

diradical character
TMM > IMA > OXA

Relative Energies and Occupation Numbers

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

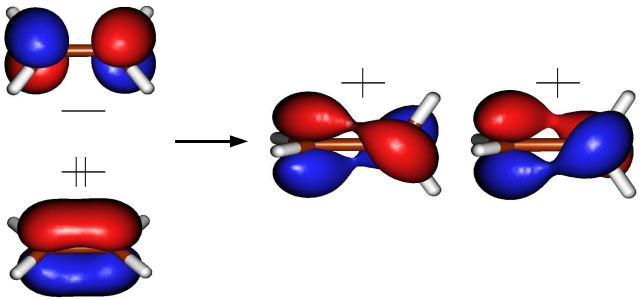
	TMM	IMA	OXA
CAS(12,12)	34.4	34.0	26.2
PNOF5	40.8	37.2	26.5
CASPT2(12,12)	43.3	39.7	32.6

Occupation numbers of the (pseudo)degenerate orbitals

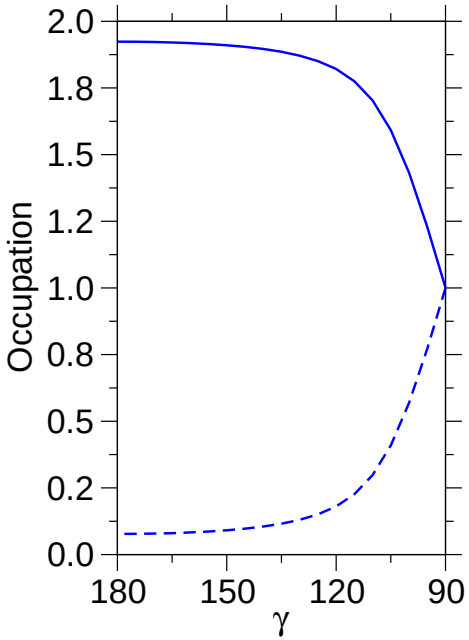
	TMM	IMA	OXA
PNOF4	1.07/0.97	1.36/0.71	1.57/0.50
PNOF5	1.00/1.00	1.26/0.74	1.46/0.54
CAS(12,12)	1.01/0.99	1.25/0.75	1.45/0.55

ChemPhysChem 12, 1673, 2011

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$(D_{2h})^\dagger$	TS $(D_{2d})^\dagger$	
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

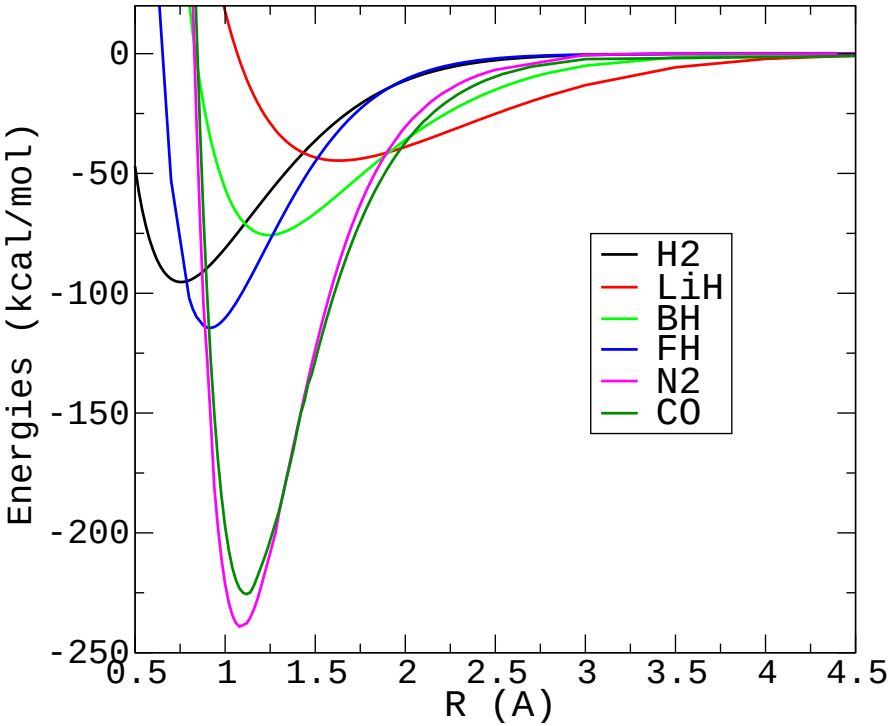
♯ cc-pVDZ Basis Set.

† 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 for diatomic molecules



BONDS

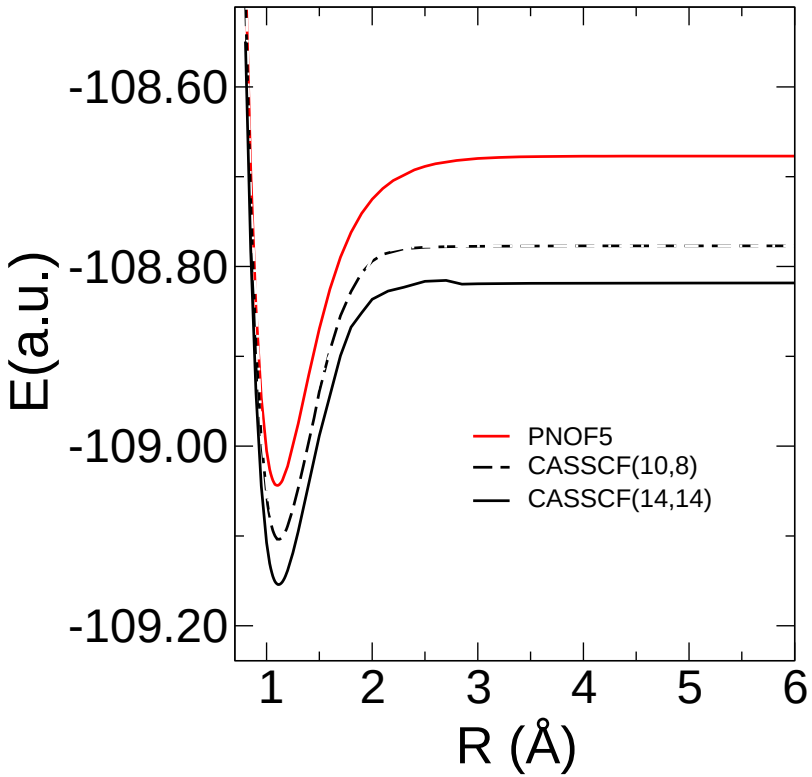
- covalent with different polarity H_2, FH, BH
- multiple bond CO, N_2
- electrostatic LiH

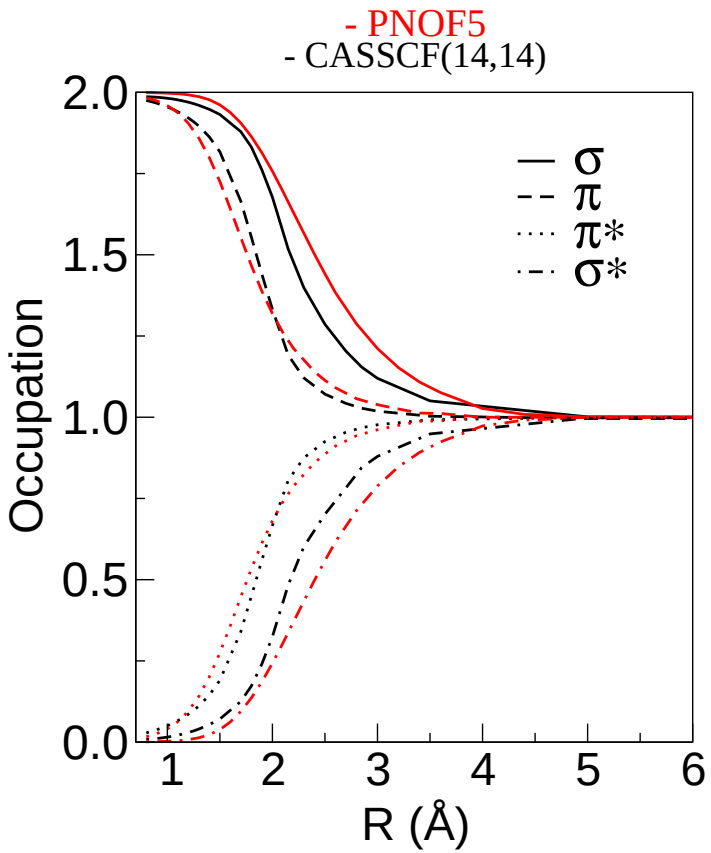
In all cases, dissociation limit implies an homolytic cleavage of the bond, high degree of near-degeneracy at the dissociation asymptote

J. Chem. Phys. 134, 164102, 2011

Dissociation for multiply bonded molecule: N_2

$$N_2(^1\Sigma) \rightarrow N(^4S) + N(^4S)$$





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

cc-pVTZ Ionization Potentials of N_2, in eV

EKT: diagonalization of the matrix ν whose elements are

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

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., 2012 (DOI: 10.1063/1.4709769)

14-electron isoelectronic series

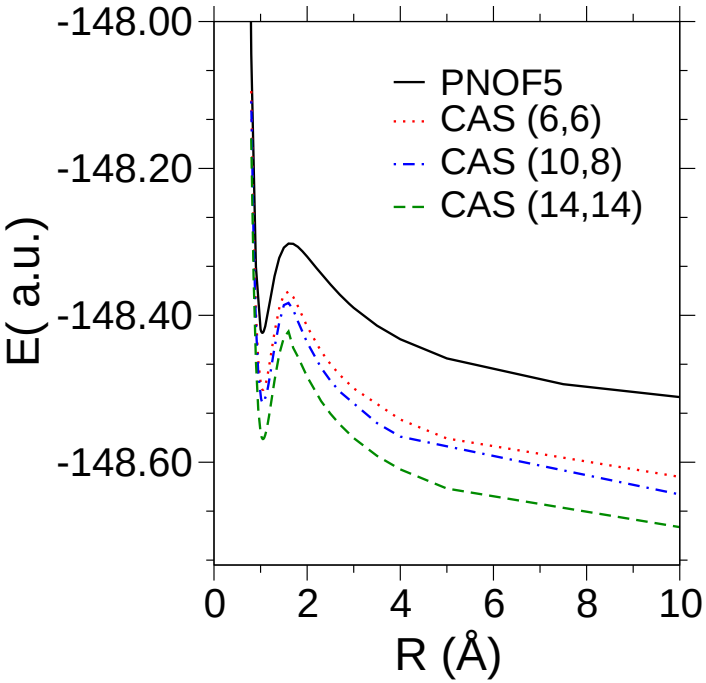
	N_2					CN^-				
	R_e	D_e	BO	μ_e	q_N	R_e	D_e	BO	μ_e	q_N
PNOF5	1.099	229.9	2.87	0.000	7	1.180	247.6	2.89	0.900	7
CAS(10,8)	1.117	205.0	2.85	0.000	7	1.200	220.0	2.86	2.241	7
CAS(14,14)	1.115	210.4	2.85	0.000	7	1.196	235.4	2.86	2.360	7
Exptl.	1.098	225.1	-	0.000	7	1.177	-	-	0.630	7

	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+}



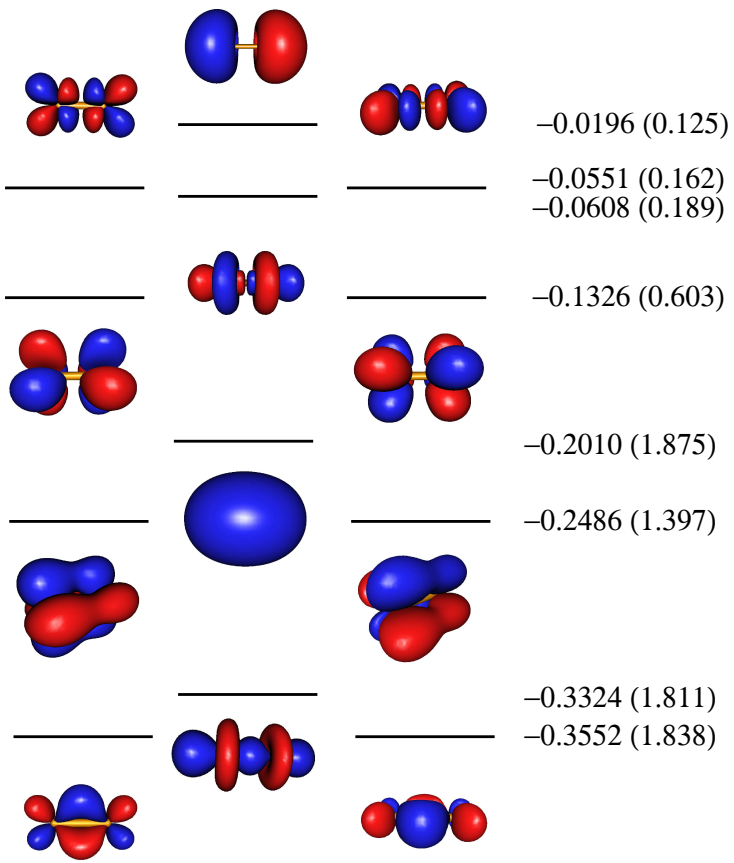
	R_e(Å)	BO	$R^{\neq}$(Å)	$\Delta E^{\neq}(\frac{kcal}{mol})$	$D_e(\frac{kcal}{mol})$	q_O
PNOF5	1.038	2.78	1.66	76.5	-71.5	7
(6,6)	1.051	2.79	1.59	83.9	-90.9	7
(10,8)	1.054	2.79	1.59	85.5	-94.8	7
(14,14)	1.052	2.79	1.59	91.9	-92.0	7
MRCI†	1.050	-	1.59	63.3	-	7

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

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

Dissociation of transition metal dimers: Cr_2, $CrMo$, Mo_2

Cr_2 at $R_e = 1.679$ Å



Effective Bond Order:

PNOF5=4.16, CASPT2=4.45

$$XY(^1\Sigma_g) \rightarrow \mathrm{X}(^7\mathrm{S}_3) + \mathrm{Y}(^7\mathrm{S}_3)$$

	CASSCF	PNOF5	CASPT2	Exp.
Cr_2	-3.38	0.84	1.50[a]	1.56
CrMo	-1.60	2.38	2.62[b]	2.09
Mo_2	0.29	2.94	4.41[c]	4.28

[a] J. Chem. Theory Comput. 7, 1640 (2011)

[b] Inorg. Chem. 50, 9219 (2011)

[c] Chem. Phys. 343, 210 (2008)

CASSCF/CASPT2: ANO-RCC-QZ, PNOF5: 6-31G

Canonical Orbitals

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

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

$$E = \mathrm{Tr}\left(\mathrm{H}\Gamma + \Lambda\right), \quad \Lambda = \{\varepsilon_{qp}\}$$

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

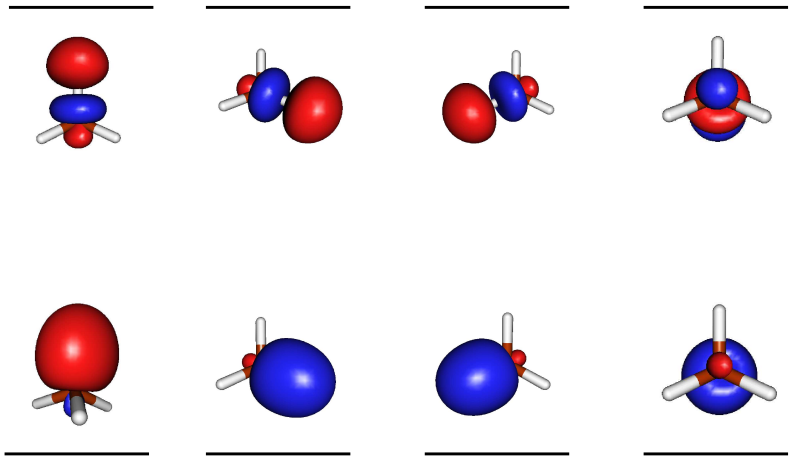
$$\mathrm{Tr}\left(\mathrm{H}\Gamma + \Lambda\right) = \mathrm{Tr}\left(\mathrm{H}'\Gamma' + \Lambda'\right),$$

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

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

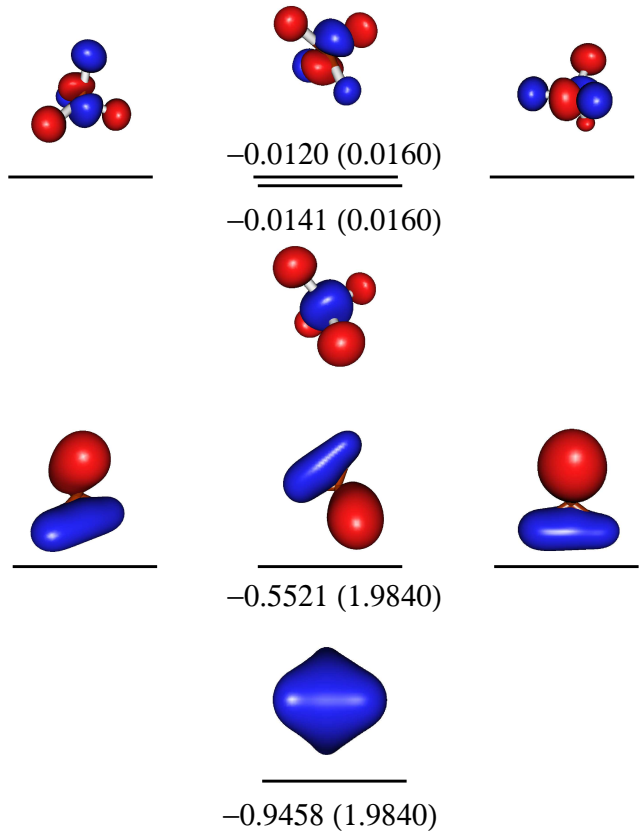
Valence orbitals of methane (CH_4)

Natural Orbital Representation



E

Canonical Orbital Representation



ChemPhysChem 2012

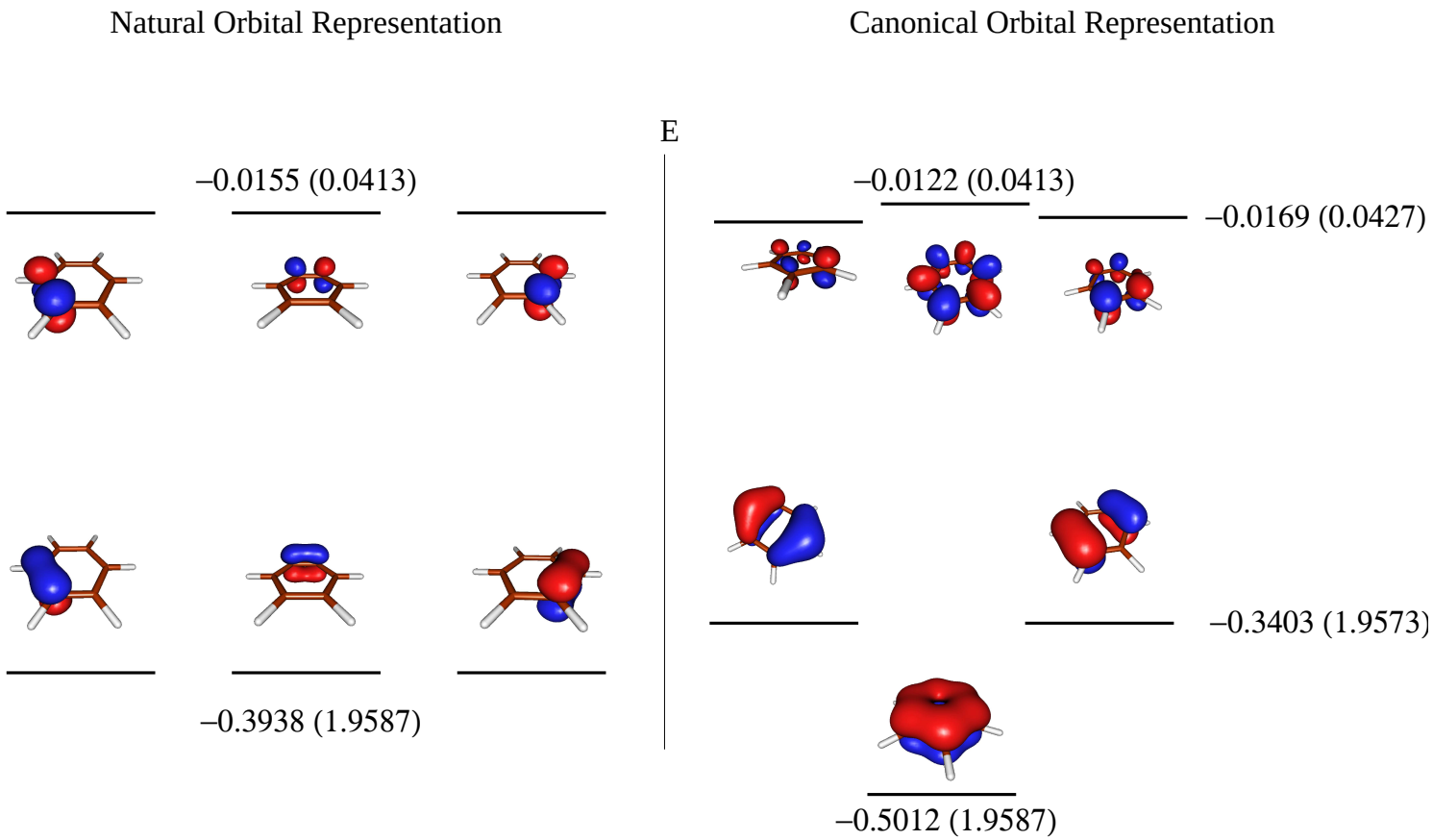
Valence vertical ionization energies, in eV, for methane

	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
OVGF	14.21	23.47
Experiment	14.40	23.00

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

Valence orbitals of Benzene (C_6H_6)



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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 37 times faster than the sequential one, in 48 processors, with an efficiency of 86%.

- the functional N-representabilty 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.

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Thank you for your attention !!!