

# New Advances in NOF Theory: PNOF5-PT2

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# Outline

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- 2 PNOF5
  - bottom-up method. Spin and N-representability conditions.
  - top-down method. The generating APSG wavefunction.
  - examples of systems where DFT yields pathological failures.
- 3 PNOF5-PT2
  - Introduction to the SC2-MCPT
  - He<sub>2</sub>, HF, CO and N<sub>2</sub>
- 4 Closing Remarks

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

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

- $\Gamma_{ki}$  : 1-RDM
- $\mathcal{H}_{ik}$ : core-Hamiltonian
- $D_{kl,ij}$  : 2-RDM
- $\langle ij|kl \rangle$ : 2e- 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  $n_i$

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

## The bottom-up and top-down methods

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum C_I(\{n_i\}) \Phi_I(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

$N$ -particle energy functional  $E[\Psi_N]$

↓

$$E[N, \{n_i, \phi_i\}]$$

↑

$$\mathbf{D}[\Gamma] = \mathbf{D}[\{n_i\}]$$

$N$ -representability conditions (D,Q,G,...)

## Cumulant expansion of the 2-RDM

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

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

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

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

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

$\Pi$  : spin-independent Hermitian matrix ( $\Pi_{pr} = \Pi_{rp}^*$ )

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

## Spin conservation rule

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

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

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

diagonal elements:  $\Delta_{pp}^{\alpha\beta} = n_p^\alpha n_p^\beta$ ,  $\Pi_{pp} = n_p$

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



# The N-representability and off-diagonal elements

## N-representability

RDMs must be derivable from an N-particle wave function  $\Psi_N$

- N-representability of  $\Gamma$ :  $0 \leq n_i \leq 1$  ( $\sum_i n_i = N$ )
- 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.

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

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

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

$$n_{p'} + n_p = 1 \quad (p' = N - p + 1)$$

$$E = \sum_{p=1}^N [n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) - \sqrt{n_{p'} n_p} \mathcal{K}_{pp'}] \\ + \sum_{p,q=1}^N '' n_q n_p (2\mathcal{J}_{pq} - \mathcal{K}_{pq}) \\ (\sum '' : q \neq p, p')$$

# Antisymmetrized Product of Strongly orthogonal Geminals

generating wavefunction of PNOF5:

$$|0\rangle = \prod_{p=1}^{N/2} \left( \sqrt{n_p} \hat{a}_p^\dagger \hat{a}_{\bar{p}}^\dagger - \sqrt{n_{p'}} \hat{a}_{p'}^\dagger \hat{a}_{\bar{p}'}^\dagger \right) |vac\rangle$$

- PNOF5 is an upper bound to the APSG energy
- separable structure  $\rightarrow$  size extensivity

$$|0\rangle = d_0 |\Psi_{HF}\rangle + \sum_{p=1}^{N/2} d_p |\Psi_{p\bar{p}}^{p'\bar{p}'}\rangle + \sum_{p<q}^{N/2} d_{pq} |\Psi_{p\bar{p}q\bar{q}}^{p'\bar{p}'q'\bar{q}'}\rangle + \dots$$

$$d_0 = \sqrt{n_1 n_2 \dots n_{N/2}}, \quad d_p = -d_0 \sqrt{\frac{n_{p'}}{n_p}}, \quad d_{pq} = d_0 \sqrt{\frac{n_{p'} n_{q'}}{n_p n_q}}, \dots$$

# APSG generating wavefunction of PNOF5

$$|0\rangle = |\Phi_0\rangle + |\Phi_d\rangle + |\Phi_q\rangle + \dots + |\Phi_{N/2}\rangle$$

where

$$|\Phi_0\rangle = d_0 |\Psi_{HF}\rangle$$

$$|\Phi_d\rangle = \sum_{p=1}^{N/2} d_p |\Psi_{p\bar{p}}^{p'\bar{p}'}\rangle$$

$$|\Phi_q\rangle = \sum_{p < q}^{N/2} d_{pq} |\Psi_{p\bar{p}q\bar{q}}^{p'\bar{p}'q'\bar{q}'}\rangle$$

...

$$|\Phi_{N/2}\rangle = d_{12\dots N/2} |\Psi_{1\bar{1}2\bar{2}\dots N/2\bar{N/2}}^{1'\bar{1}'2'\bar{2}'\dots N/2'\bar{N/2}'}\rangle$$

$|0\rangle$  is a restricted coupled cluster

## spin-parallel and spin-opposite components of the 2-RDM

$$D_{pq,rt} = \frac{n_p n_q}{2} (\delta_{pr} \delta_{qt} - \delta_{pt} \delta_{qr}) (1 - \delta_{qp}) (1 - \delta_{qp'})$$

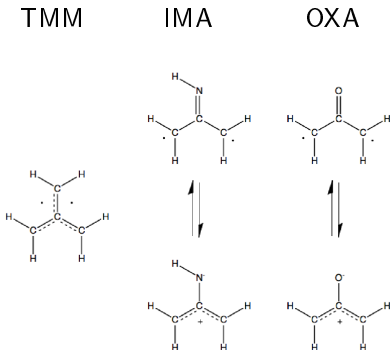
$$D_{p\bar{q},r\bar{t}} = \frac{n_p n_q}{2} \delta_{pr} \delta_{qt} (1 - \delta_{qp}) (1 - \delta_{qp'}) \\ + \left( \frac{n_p}{2} \delta_{rp} - \frac{\sqrt{n_p n_{p'}}}{2} \delta_{rp'} \right) \delta_{pq} \delta_{rt}$$

PNOF5:

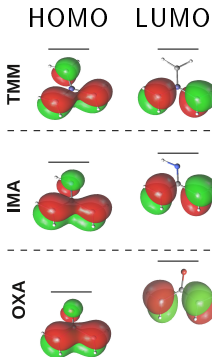
$$E = \sum_{p=1}^N [n_p (2\mathcal{H}_{pp} + \mathcal{J}_{pp}) - \sqrt{n_{p'} n_p} \mathcal{K}_{pp'}] \\ + \sum_{p,q=1}^N " n_q n_p (2\mathcal{J}_{pq} - \mathcal{K}_{pq})$$

Pernal, Comput. Theor. Chem. 1003, 127 (2013)

# Planar trimethylenemethane



TMM: trimethylenemethane  
 IMA: iminoallyl diradicaloid  
 OXA: oxyallyl diradicaloid



diradical character  
 TMM > IMA > OXA

# Relative Energies and Occupation Numbers

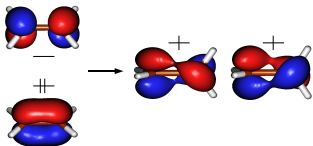
Relative energy with respect to its cyclic isomer, in kcal/mol

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

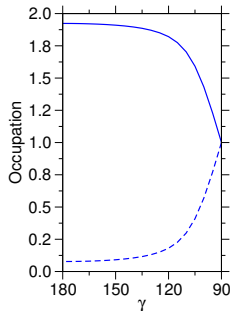
Occupation numbers of the (pseudo)degenerate orbitals

	TMM	IMA	OXA
<b>PNOF4</b>	<b>1.07/0.97</b>	<b>1.36/0.71</b>	<b>1.57/0.50</b>
<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



Natural Orbital Functional Theory correctly describes degeneracy effects in diradical reactions



J. Chem. Phys. 134, 164102, 2011



## Ethylene Torsion. Energetics

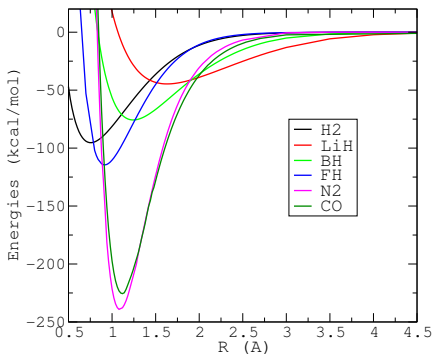
	$E$ (Hartrees)		$\Delta E$ (kcal/mol)
	Min( $D_{2h}$ ) <sup>†</sup>	TS ( $D_{2d}$ ) <sup>†</sup>	
CASPT2(12,12)	-78.342567	-78.238122	65.5
PNOF5	-78.136524	-78.032063	65.6
B3LYP <sup>‡</sup>	-78.591976	-78.490308	63.8
PBE0 <sup>‡</sup>	-78.485589	-78.388529	60.9
M06-2X <sup>‡</sup>	-78.543689	-78.437072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

‡ cc-pVDZ Basis Set.

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

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

## cc-pVTZ dissociation curves for diatomic molecules



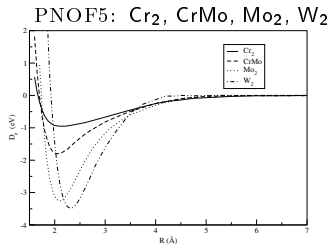
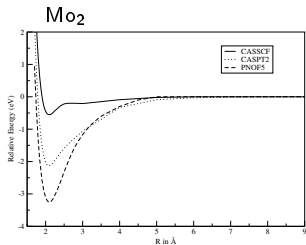
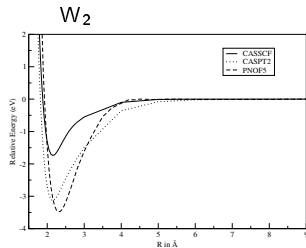
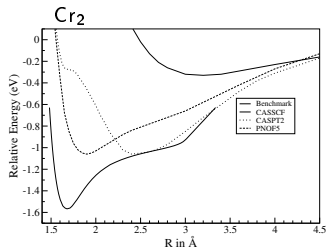
### BONDS

- covalent  $H_2$ ,  $FH$ ,  $BH$
- multiple bond  $CO$ ,  $N_2$
- electrostatic  $LiH$

Integer number of electrons  
on dissociated atoms

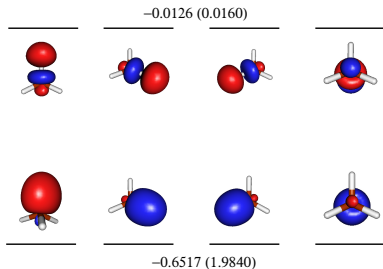
In all cases, dissociation limit implies an homolytic cleavage of the bond, high degree of near-degeneracy at the dissociation asymptote

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



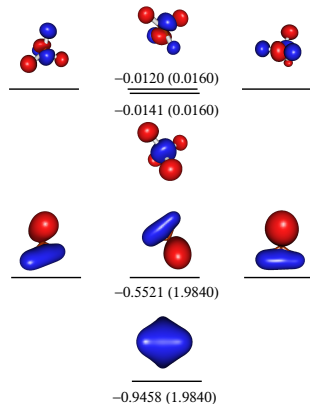
# Valence orbitals of methane ( $CH_4$ )

Natural Orbital Representation

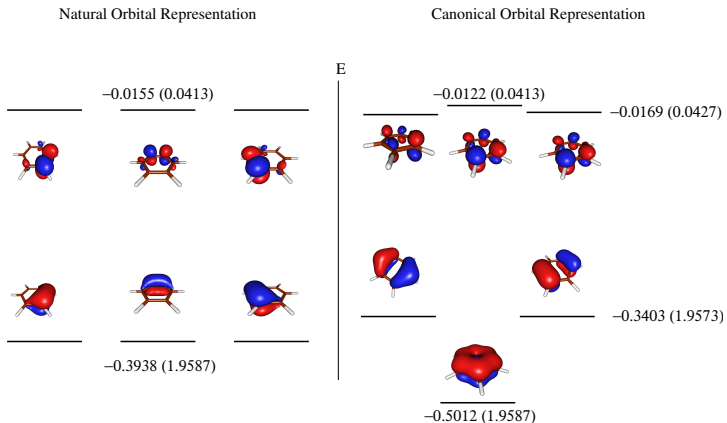


Canonical Orbital Representation

E

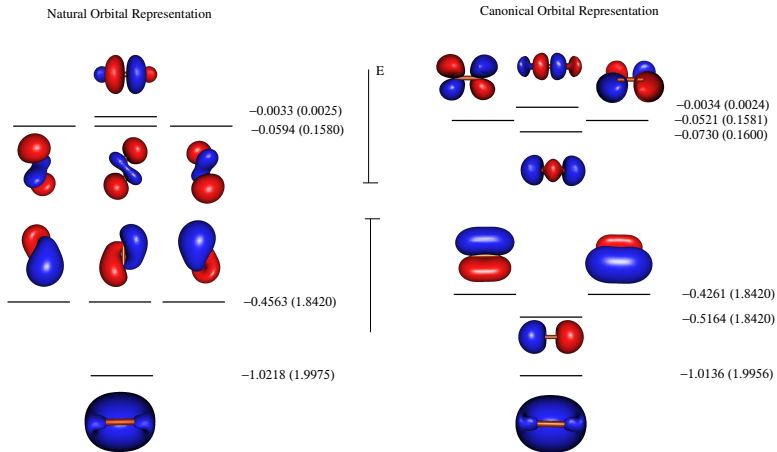


# Valence orbitals of Benzene ( $C_6H_6$ )



ChemPhysChem 13, 2297, 2012, Theor. Chem. Acc. 132, 1298 (2013).

# Valence orbitals of carbon dimer ( $C_2$ )



J. Chem. Phys. 138, 151102 (2013).



# The reciprocal space in the MCPT

MCPT:

- $|0\rangle$ : the zero-order ground state
- one seeks perturbative corrections to  $|0\rangle$
- overlapping basis in the full M-dimensional space

$$|K\rangle = \begin{cases} |0\rangle, & K = 0 \\ |\Psi_K\rangle, & K \neq 0 \end{cases}$$

$|\Psi_K\rangle$ : excited determinants with respect to  $|\Psi_{HF}\rangle$

- reciprocal (biorthogonal) vectors

$$\langle \tilde{K} | = \begin{cases} d_0^{-1} \langle \Psi_{HF} |, & K = 0 \\ \langle \Psi_K | - d_K \langle \tilde{0} |, & K \neq 0 \end{cases}$$

$$\langle \tilde{K} | L \rangle = \delta_{KL}$$

## Non-Hermitian zero-order Hamiltonian

- Spectral resolution:

$$\hat{H}^0 = \sum_{K=0}^M E_K |K\rangle \langle \tilde{K}|$$

- $\{|K\rangle\}$  are right and  $\{\langle \tilde{K}|\}$  are left eigenvectors of  $\hat{H}^0$
  - $E_K$ -s are free parameters, define the partitioning
  - size-consistency is ensured by omitting projectors
- $E_0$  is conveniently taken as the zero-order ground state energy:

$$E_0 = E^{(0)} = \langle \tilde{0} | \hat{H} | 0 \rangle = \tilde{E}_{HF} + \tilde{E}_{corr}$$

$$\tilde{E}_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle, \quad \tilde{E}_{corr} = - \sum_{p=1}^{N/2} \sqrt{\frac{n_{p'}}{n_p}} \mathcal{K}_{pp'}$$



## The Davidson-Kapuy Partitioning: SC2-MCPT.

- The zero-order excited energies:  $E_K = E_0 + \Delta_K$

$$\Delta_K = \begin{cases} \varepsilon_s - \varepsilon_a & a \leq N ; s > N \\ \varepsilon_s + \varepsilon_u - \varepsilon_a - \varepsilon_b & a, b \leq N ; s, u > N \\ \dots & \dots \end{cases}$$

$\Delta_K$  : differences between diagonal elements of Fock operator

$$\varepsilon_i = h_{ii} + \sum_{q=1}^{N/2} [2 \langle iq | iq \rangle - \langle iq | qi \rangle]$$

size-consistency is ensured by considering energy denominators as differences of one-particle energies

A. Szabados, et. al., J. Chem. Phys. 122, 114104 (2005).

## Lowest order energy corrections

$$E^{(1)} = \langle \tilde{0} | \hat{V} | 0 \rangle = 0, \quad \hat{V} = \hat{H} - \hat{H}^0$$

$$\begin{aligned} E^{(2)} &= - \sum_{K=1}^M \frac{\langle \tilde{0} | \hat{V} | K \rangle \langle \tilde{K} | \hat{V} | 0 \rangle}{E_K - E_0} = - \sum_{K=1}^M \frac{\langle \tilde{0} | \hat{H} | K \rangle \langle \tilde{K} | \hat{H} | 0 \rangle}{\Delta_K} \\ &= \sum_{K=1}^M \frac{\langle \Psi_{HF} | \hat{H} | K \rangle [d_K E^{(0)} - \langle K | \hat{H} | 0 \rangle]}{d_0 \Delta_K} \end{aligned}$$

- non-invariance with respect to the choice of the Fermi vacuum
- one needs to consider only  $\{|\Psi_a^s\rangle\}$  and  $\{|\Psi_{ab}^{su}\rangle\}$  excited det.

## Second-order energy correction

$$E^{(2)} = E_0^{(2)} + E_d^{(2)} + E_q^{(2)}$$

where

$$E_0^{(2)} = 2 \sum_{pr}^{N/2} \frac{|f_{pr}|^2}{\epsilon_p - \epsilon_r} + \sum_{pqrt}^{N/2} \frac{\langle pq | rt \rangle [2 \langle rt | pq \rangle - \langle rt | qp \rangle]}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_t}$$

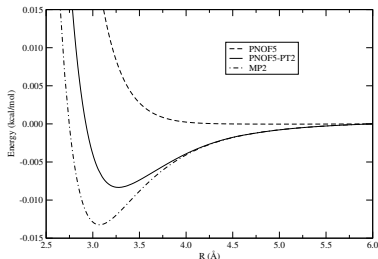
$$E_q^{(2)} = \sum_p^{N/2} \binom{n_{p'}}{n_p} \frac{|\mathcal{K}_{pp'}|^2}{(\epsilon_{p'} - \epsilon_p)} + \sum_{pq}^{N/2} \sqrt{\frac{n_{p'} n_{q'}}{n_p n_q}} \frac{[2 \langle pq | p'q' \rangle - \langle pq | q'p' \rangle]^2}{\epsilon_p + \epsilon_q - \epsilon_{p'} - \epsilon_{q'}}$$

## Second-order energy correction

$$\begin{aligned}
 E_d^{(2)} = & 2 \sum_p^{N/2} \sqrt{\frac{n_{p'}}{n_p}} \frac{|f_{pp'}|^2}{(\varepsilon_{p'} - \varepsilon_p)} + 2 \sum_{pqr}^{N/2} \sqrt{\frac{n_r}{n_{r'}}} \frac{\langle pq | rr \rangle \langle r' r' | pq \rangle}{2\varepsilon_r - \varepsilon_p - \varepsilon_q} \\
 & + 2 \sum_{pr}^{N/2} \frac{f_{rp}}{\varepsilon_r - \varepsilon_p} \left[ \sqrt{\frac{n_{p'}}{n_p}} \langle pr | p' p' \rangle - \sqrt{\frac{n_r}{n_{r'}}} \langle r' r' | pr \rangle \right] \\
 & + 2 \sum_p^{N/2} \sqrt{\frac{n_{p'}}{n_p}} \left\{ \sum_r^{N/2} \frac{f_{rp'} \langle pp | p' r \rangle}{\varepsilon_r + \varepsilon_{p'} - 2\varepsilon_p} + \sum_q^{N/2} \frac{f_{qp} \langle pq | p' p' \rangle}{\varepsilon_p + \varepsilon_q - 2\varepsilon_{p'}} \right. \\
 & + \frac{1}{2} \sum_{rs}^{N/2} \frac{\langle pp | rs \rangle \langle rs | p' p' \rangle}{\varepsilon_r + \varepsilon_s - 2\varepsilon_p} + \sum_{qr}^{N/2} \frac{\langle pq | rp' \rangle \langle pr | qp' \rangle}{\varepsilon_p + \varepsilon_q - \varepsilon_r - \varepsilon_{p'}} \\
 & \left. + \sum_{qr}^{N/2} \frac{[\langle pq | rp' \rangle + \langle pr | qp' \rangle] \langle pq | p' r \rangle}{\varepsilon_p + \varepsilon_q - \varepsilon_r - \varepsilon_{p'}} \right\}
 \end{aligned}$$

## Dissociation of the helium dimer (aug-cc-pV5Z)

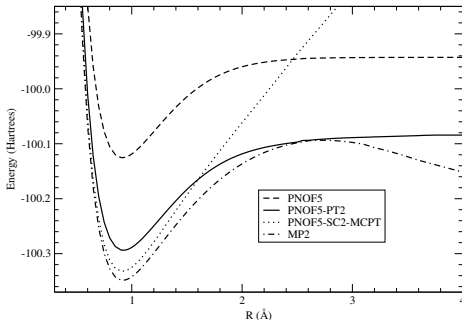
- PNOF5 curve is repulsive (no correlation between pairs)
- the interpair correlation should be mostly dispersion type
- MCPT predicts several local minima (not shown)
- double excitations  $|\Psi_{p\bar{p}}^{su}\rangle$  are excluded from  $E^{(2)} \Rightarrow$  PNOF5-PT2



$$D_e = 0.009 \text{ kcal/mol}$$

$$D_e + 1/3 D_e = 0.012 \text{ kcal/mol} \\ \approx D_e^{MP2}$$

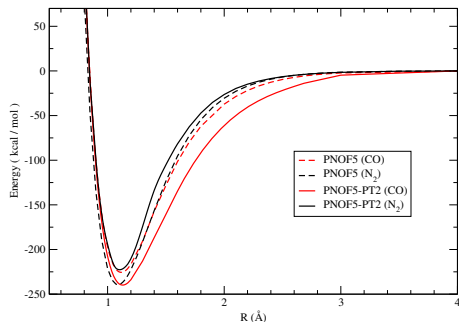
# Dissociation curves of the hydrogen fluoride (cc-pVTZ)



	$D_e$ (kcal/mol)
PNOF5	114.5
PNOF5-PT2	134.2
Experiment	141.1

- the excitations between the lowest-weakly and highest-strongly occupied orbitals, which in the limit correspond to the degenerate orbitals, are removed from the whole dissociation process.

# Dissociation of the CO and N<sub>2</sub> molecules (cc-pVTZ)



	$D_e(N_2)$	$D_e(CO)$
PNOF5	239.3	225.6
PNOF5-PT2	221.8	238.0
Experiment	225.1	256.2

- PNOF5 shows a wrong order :  $D_e(CO) < D_e(N_2)$ .
- PNOF5-PT2 recovers the correct order  $D_e(N_2) < D_e(CO)$ .

## Selected molecular properties: $R_e$ , $D_e$ , $\omega_e$

Mol	PNOF5			PNOF5-PT2			Experimental		
	$R_e$	$\omega_e$	$D_e$	$R_e$	$\omega_e$	$D_e$	$R_{exp}$	$\omega_e$	$D_e$
HF	0.915	4149.3	114.5	0.924	4047.0	134.2	0.917	4138.4	141.1
N <sub>2</sub>	1.090	2468.7	239.3	1.103	2326.3	221.8	1.098	2358.6	225.1
CO	1.116	2313.8	225.6	1.129	2199.0	238.0	1.128	2169.8	256.2

- PNOF5 underestimates  $R_e$  and overestimates  $\omega_e$ .
- PNOF5-PT2 increases the predicted equilibrium bond lengths.
- For frequencies, the PNOF5-PT2 values decrease toward the experimental data, in particular in case of multiple bonds.
- PNOF5-PT2 dissociation energies have improved substantially over the PNOF5 ones, getting closer to the experimental marks.



## Closing Remarks

- the generating PNOF5-wavefunction is a two-configuration APSPG (GVB or PP). It has been shown that PNOF5 can be obtained by top-down and bottom-up methods.
- a computationally tractable second-order perturbation theory PNOF5-PT2 has been derived from the SC2-MCPT. This ansatz involves only double excitations from different spatial orbitals to account for the interpair correlation.
- future work: better description of the intrapair electron correlation with an extended version of PNOF5

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Thank you for your attention !!!