

The intra-pair and inter-pair electron correlation in NOFT

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Outline

- 1 Introduction to the Natural Orbital Functional Theory (NOFT)
- 2 The intrapair electron correlation: PNOF5e
 - Examples: H_2 , LiH , Li_2 , H_3^+ , C_2H_4 , Cr_2
- 3 The interpair electron correlation: PNOF5-PT2
 - Examples: He_2 , CO , N_2
- 4 Closing Remarks

J. Chem. Phys. 139, 064111, 2013; J. Mol. Phys. 2013

The exact energy functional

Consider an N-electron molecule described by a non-degenerate state Ψ .

\hat{H} has only one- and two-particle operators, so the electronic energy in the BO approximation is an explicitly known functional of the spinless 1- and 2-RDMs:

$$E[N, \Gamma, D] = -\frac{1}{2} \int \nabla_1^2 \Gamma(\mathbf{r}'_1, \mathbf{r}_1) |_{\mathbf{r}'_1=\mathbf{r}_1} d\mathbf{r}_1 + \int \Gamma(\mathbf{r}_1, \mathbf{r}_1) v(\mathbf{r}_1) d\mathbf{r}_1 \\ + \int \frac{D(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$\Gamma(\mathbf{r}'_1, \mathbf{r}_1) = N \sum_{\sigma_1} \int \Psi^*(\mathbf{r}'_1, \sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{r}_1, \sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N$$

$$D(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \sum_{\sigma_1, \sigma_2} \int |\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{x}_3, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_3 \dots d\mathbf{x}_N$$

$$\Gamma(\mathbf{x}'_1, \mathbf{x}_1) = \frac{2}{N-1} \int D(\mathbf{x}'_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_2 \quad \Rightarrow \quad E[N, \Gamma, D] = E[N, D]$$

The variational approach in quantum chemistry

- The wavefunction theories (CI, CC, ...)

- Fundamental Variable: $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) \Rightarrow D_\Psi$ (by contraction)

- The ground-state energy: $E_0 = \inf_{\Psi \in \mathcal{L}_N} E[\Psi] = E[\Psi_0] \equiv E[N, D_{\Psi_0}]$

- The variational theories without wavefunction

Method :	DFT	1DMFT		2DMFT
Variable :	$\rho_\Psi(\mathbf{r})$	$\Gamma_\Psi(\mathbf{x}'_1, \mathbf{x}_1)$		$D_\Psi(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2)$
			(reconstruction)	
Functional :	$E_\Psi[N, \rho_\Psi]$	$E_\Psi[N, \Gamma_\Psi]$	\implies	$E[N, D_\Psi]$
	(HK)	(Gilbert)		(exact)

The N-representability Problem in DFT and 1DMT

- ① The N-representability of $\rho(\Gamma)$: $\rho_{\Psi}(\Gamma_{\Psi}), \Psi \Leftrightarrow \rho(\Gamma)$

- the necessary and sufficient conditions are known

- DFT: $\rho \geq 0, \int \rho(\mathbf{r}) d\mathbf{r} = N$
- 1DMFT: $0 \leq \Gamma \leq ql, \text{Tr}(\Gamma) = N$

- ② The functional N-representability: $E_{\Psi}[N, \rho_{\Psi}] (E_{\Psi}[N, \Gamma_{\Psi}])$

$$E[\Psi] = E[D_{\Psi}] \Leftrightarrow E[\rho_{\Psi}] (E[\Gamma_{\Psi}])$$

- some practical necessary conditions known for the 2-RDM

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

Natural Orbitals and Occupation Numbers

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

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

$\phi_i(\mathbf{x})$: natural spin-orbital

n_i : occupation number

- $E_\Psi[N, \Gamma_\Psi] \Rightarrow E_\Psi[N, \{n_i, \phi_i\}]$
- necessary and sufficient conditions for N-representability of Γ :

$$0 \leq n_i \leq 1, \quad \sum_i n_i = N$$

The electronic energy in NOFT

The energy $E[N, \Gamma, D]$ is expressed in terms of the diagonal 1-RDM:

$$E[N, \{n_i, \phi_i\}] = \sum_i n_i \mathcal{H}_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l] \langle kl | ij \rangle$$

- \mathcal{H}_{ii} : core-Hamiltonian
- $\{n_i\}$: occupation numbers
- $\langle kl | ij \rangle$: 2e- integrals
- $\{\phi_i(\mathbf{x})\}$: natural orbitals

2-RDM: $D[n_i, n_j, n_k, n_l] \Leftarrow$ reconstruction functional

Advantage of NOFT with respect to DFT

the kinetic energy is explicitly defined and
does not require the construction of a functional

Cumulant expansion of the 2-RDM

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

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

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

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

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

Sum Rules: $\sum_{q \neq p} \Delta_{pq}^{\sigma\sigma} = n_p^\sigma (1 - n_p^\sigma)$, $\sum_q \Delta_{pq}^{\alpha\beta} = \Pi_{pp}$

Π : spin-independent Hermitian matrix

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

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

1 spin-restricted formalism:

- $|\phi_i\rangle = |\varphi_p\rangle \otimes |\sigma\rangle, \quad \varphi_p(\mathbf{r}) = \varphi_p^\alpha(\mathbf{r}) = \varphi_p^\beta(\mathbf{r})$

- $n_p^\alpha = n_p^\beta = n_p, \quad 2 \sum_p n_p = N$

- $\Delta_{pq}^{\alpha\alpha} = \Delta_{pq}^{\alpha\beta} = \Delta_{pq}^{\beta\alpha} = \Delta_{pq}^{\beta\beta} = \Delta_{pq}$

2 $\langle \widehat{S}^2 \rangle = 0 \Rightarrow \Delta_{pp} = n_p^2, \Pi_{pp} = n_p$ (J. Chem. Phys. 131, 021102, 2009).

$$\Delta_{pq} = n_p^2 \delta_{pq} + \Delta(n_p, n_q)(1 - \delta_{pq}), \quad \sum_q \Delta_{pq} = n_p$$

$$\Pi_{pq} = n_p \delta_{pq} + \Pi(n_p, n_q)(1 - \delta_{pq})$$

The N-representability and off-diagonal elements

- 1 Analytic constraints imposed by necessary positivity conditions of the 2-matrix N-representability

- $D \geq 0, Q \geq 0$

$$\Delta(n_p, n_q) \leq n_p n_q, \quad \Delta(n_p, n_q) \leq h_p h_q \quad (h_p = 1 - n_p)$$

- $G \geq 0$

$$\Pi^2(n_p, n_q) \leq n_p h_p n_q h_q + \Delta(n_p, n_q) [n_p h_q + h_p n_q] + \Delta^2(n_p, n_q)$$

J. Chem. Phys. 133, 111101 (2010).

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

strengths and weaknesses: Int. J. Quantum Chem. 113, 620, 2013

- PNOF5e

Δ - and Π -matrices for PNOF5e ($p \neq q$)

$$\Delta(n_p, n_q) = n_p n_q \delta_{p\Omega_g} \delta_{q\Omega_g}, \quad \delta_{p\Omega_g} = \begin{cases} 1, & p \in \Omega_g \\ 0, & p \notin \Omega_g \end{cases}$$

$$\Pi(n_p, n_q) = \delta_{p\Omega_g} \delta_{q\Omega_g} \begin{cases} -\sqrt{n_p n_q}, & p=g \text{ or } q=g \\ \sqrt{n_p n_q}, & p, q > N/2 \end{cases}$$

- Ω_g is a subspace containing an orbital g below the Fermi level ($g \leq N/2$), and several orbitals with $p > N/2$.
- subspaces are mutually disjoint: $\Omega_{g1} \cap \Omega_{g2} = \emptyset$
- sum rule: $\sum_q \Delta_{pq} = n_p \rightarrow \sum_{q \in \Omega_g} n_q = 1 \quad (g = 1, \dots, N/2)$

Note: If $(p \in \Omega_{g1}) \cap (q \in \Omega_{g2}) \rightarrow \Delta, \Pi = 0 \rightarrow D^{HF}$

The energy functional for PNOF5e

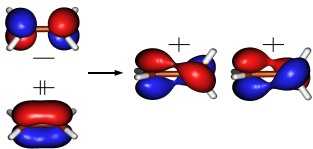
$$E = \sum_{g=1}^{N/2} E_g(2e^-) + \sum_{f \neq g}^{N/2} \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} n_p n_q (2\mathcal{J}_{qp} - \mathcal{K}_{qp})$$

$$E_g(2e^-) = 2 \sum_{p \in \Omega_g} n_p \mathcal{H}_{pp} + \sum_{p, q \in \Omega_g} \Pi_{pq}(2e^-) \mathcal{K}_{qp} = 2 \sum_{p \in \Omega_g} n_p \mathcal{H}_{pp} \\ + n_g \mathcal{J}_{gg} - 2 \sum_{q \in \Omega'_g} \sqrt{n_g n_q} \mathcal{K}_{qg} + \sum_{p, q \in \Omega'_g} \sqrt{n_p n_q} \mathcal{K}_{qp}$$

- PNOF5: $\Omega_g = (g, g')$, $n_g + n_{g'} = 1$
- Solution: self-consistent iterative diagonalization procedure

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

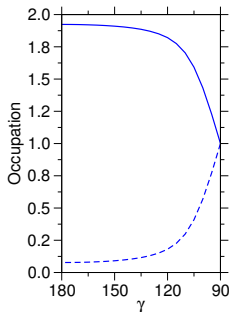
Ethylene Torsion (cc-pVDZ)



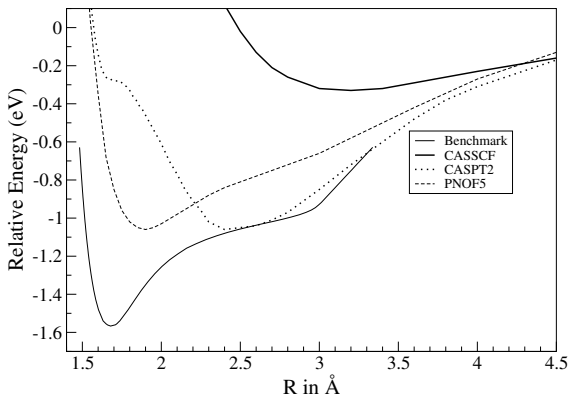
Natural Orbital Functional Theory correctly describes degeneracy effects in diradical reactions

	ΔE (kcal/mol)
CASPT2(12,12)	65.5
PNOF5	65.6
B3LYP [‡]	63.8
PBE0 [‡]	60.9
M06-2X [‡]	66.9

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

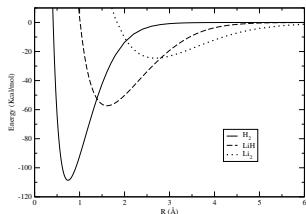


J. Chem. Phys. 134, 164102, 2011

Dissociation of transition metal dimers (Cr_2)

(14s11p6d3f)/[8s6p4d1f] basis set

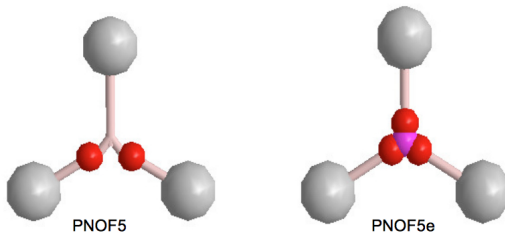
Dissociation curves for H₂, LiH and Li₂ (aug-cc-pVTZ)



	PNOF5		PNOF5e		Exp.	
	R _e	D _e	R _e	D _e	R _e	D _e
H ₂	0.756	95.4	0.743	108.6	0.743	109.5
LiH	1.631	44.7	1.613	57.3	1.595	58.0
Li ₂	2.703	12.6	2.692	24.6	2.673	24.4

	PNOF5			PNOF5e			Exp.		
	ω_e	$\omega_e X_e$	$\omega_e Y_e$	ω_e	$\omega_e X_e$	$\omega_e Y_e$	ω_e	$\omega_e X_e$	$\omega_e Y_e$
H ₂	4221.7	124.3	0.5	4395.0	121.6	0.8	4401.2	121.3	0.8
LiH	1306.0	24.2	0.2	1382.3	21.7	0.2	1405.5	23.2	0.2
Li ₂	354.7	-66.9	-14.4	348.5	3.9	0.1	351.4	2.6	0.0

Properties of BCPs and NNM of the H_3^+ cluster (cc-pVTZ)



NOF	#	ϵ	Bond Strain
PNOF5	2	3.3104 ± 0.0000	0.2294 ± 0.0000
PNOF5e	3	1.8737 ± 0.0085	0.0000 ± 0.0000

the values of ρ , $\nabla^2\rho$ and energy densities G and H, are similar

Errors in total energies (kcal/mol)

	PNOF5	PNOF5e	CCSD(T)*
H ₂	13.2	0.0	-1.172756
LiH	19.9	2.3	-8.048590
Li ₂	26.7	4.8	-14.954066

* reference values at the equilibrium bond length in Hartrees

aug-cc-pVTZ basis set

The bottom-up and top-down methods

(J. Mod. Phys. 4, 391, 2013)

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

$$E[\Psi] \equiv E[N, D_\Psi]$$

↓

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

↑

$$D[n_i, n_j, n_k, n_l]$$

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

A generating wavefunction of PNOF5e (APSG)

$$|0\rangle = \prod_{g=1}^{N/2} \hat{\psi}_g^\dagger |vac\rangle = \prod_{g=1}^{N/2} \left(\sqrt{n_g} \hat{a}_g^\dagger \hat{a}_{\bar{g}}^\dagger - \sum_{p \in \Omega'_g} \sqrt{n_p} \hat{a}_p^\dagger \hat{a}_{\bar{p}}^\dagger \right) |vac\rangle$$

$$\sum_{p \in \Omega_g} n_p = 1, \quad \Omega_{g1} \cap \Omega_{g2} = \emptyset$$

$$E^{exact} \leq E^{APSG} [\{c_p\}, \{\varphi_p\}] \leq E^{PNOF5e} [\{n_p\}, \{\varphi_p\}]$$

$$\text{PNOF5: } |0\rangle = \prod_{g=1}^{N/2} \left(\sqrt{n_g} \hat{a}_g^\dagger \hat{a}_{\bar{g}}^\dagger - \sqrt{n_{g'}} \hat{a}_{g'}^\dagger \hat{a}_{\bar{g}'}^\dagger \right) |vac\rangle \quad (\text{GVB-PP})$$

(Pernal, Comput. Theor. Chem. 1003, 127, 2013; Piris, J. Chem. Phys. 139, 064111, 2013)

APSG generating wavefunction of PNOF5

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

$$|\Phi_0\rangle = d_0 |\Psi_{HF}\rangle \qquad |\Phi_d\rangle = -\sum_{g=1}^{N/2} \sum_{p \in \Omega'_g} d_g^p |\Psi_{g\bar{g}}^{p\bar{p}}\rangle$$

$$|\Phi_q\rangle = \sum_{g < f}^{N/2} \sum_{p \in \Omega'_g} \sum_{q \in \Omega'_f} d_{gf}^{pq} |\Psi_{g\bar{g}f\bar{f}}^{p\bar{p}q\bar{q}}\rangle$$

...

$$|\Phi_{N/2}\rangle = (-1)^{\frac{N}{2}} \sum_{p \in \Omega'_1} \sum_{q \in \Omega'_2} \dots \sum_{r \in \Omega'_{N/2}} d_{12\dots N/2}^{pq\dots r} |\Psi_{1\bar{1}2\bar{2}\dots N/2\bar{N/2}}^{p\bar{p}q\bar{q}\dots r\bar{r}}\rangle$$

$$d_0 = \sqrt{n_1 n_2 \dots n_{N/2}}, \quad d_g^p = d_0 \sqrt{\frac{n_p}{n_g}}, \quad d_{gf}^{pq} = d_0 \sqrt{\frac{n_p n_q}{n_g n_f}}, \quad \dots$$

Advantages of the SC2-MCPT

- no need to solve a system of linear equations for the corrections
- The resulting work formulas involve only matrix elements between pure determinants like occurs in the standard single-reference perturbation theory
- the size-consistency is ensured

Z. Rolik, et. al., J. Chem. Phys. 119, 1922 (2003)

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

The reciprocal space in the 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

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

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
 - size-consistency is ensured by omitting projectors
 - E_K -s are free parameters, define the partitioning
- E_0 is conveniently taken as the zero-order ground state energy:

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

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

The Davidson-Kapuy Partitioning: SC2-MCPT.

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

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

Δ_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

Lowest order energy corrections

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

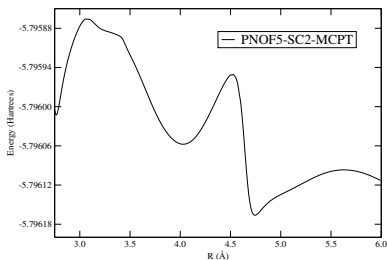
$$E^{(2)} = - \sum_{K=1}^M \frac{\langle \tilde{0} | \hat{V} | K \rangle \langle \tilde{K} | \hat{V} | 0 \rangle}{E_K - E_0} = - \sum_{K=1}^M \frac{\langle \tilde{0} | \hat{H} | K \rangle \langle \tilde{K} | \hat{H} | 0 \rangle}{\Delta_K}$$

$$= \sum_{K=1}^M \frac{\langle \Psi_{HF} | \hat{H} | K \rangle \left[d_K E^{(0)} - \langle K | \hat{H} | 0 \rangle \right]}{d_0 \Delta_K} = E_0^{(2)} + E_d^{(2)} + E_q^{(2)}$$

- 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.
- $E_0^{(2)}$ is exactly the same as in the Møller-Plesset PT

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

- typical phenomenon of dispersion interaction ($E_b = 0.021$ kcal/mol)
- the interpair correlation is responsible for dispersion



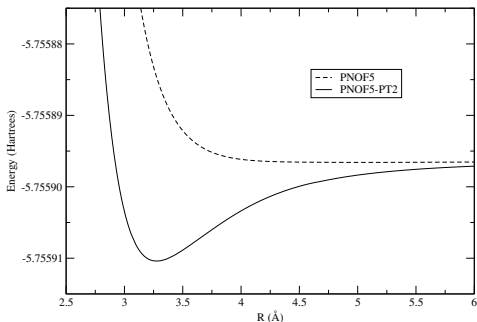
full CI calculations (JCP 137, 204117, 2012)

- contribution of $|\Psi_{ab}^{su}\rangle$ with $a \neq b$:
2/3 \approx 100% of vdW for same-spin e^-
1/3 \rightarrow 50% of vdW for opposite-spin e^-
- contribution of $|\Psi_{p\bar{p}}^{su}\rangle$:
50% of vdW for opposite-spin e^-

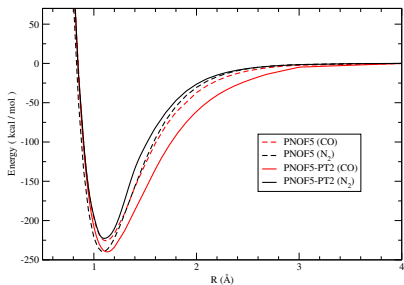
Note: excitations $|\Psi_{p\bar{p}}^{su}\rangle$ are already in $|0\rangle$

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

- PNOF5 curve is repulsive (no correlation between pairs)
- PNOF5-PT2: $|\Psi_{p\bar{p}}^{su}\rangle$ are excluded from $E^{(2)}$
- dissociation limit = $2 \times E(\text{He}) \rightarrow$ size-consistency of the method



Dissociation of the CO and N₂ molecules (cc-pVTZ)



- PNOF5: $D_e(\text{CO}) < D_e(\text{N}_2)$
- PNOF5-PT2: $D_e(\text{N}_2) < D_e(\text{CO})$

Mol	PNOF5			PNOF5-PT2			Exp.		
	R_e	ω_e	D_e	R_e	ω_e	D_e	R_{exp}	ω_e	D_e
N ₂	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

Conclusions

- A NOF based on an explicit reconstruction of the 2-RDM in terms of the ONs has been proposed. This functional describes the static (non-dynamic) and intrapair dynamic correlations.
- The bottom-up method: cumulant expansion imposing the D, Q and G necessary N-representability conditions of 2-RDM
- The top-down method: a generating PNOF5e-wavefunction of APSG type with expansion coefficients expressed by the ONs
- PNOF5-PT2: a computationally tractable second-order PT with PNOF5 as a reference was derived based on SC2-MCPT. This ansatz involves only double excitations from different spatial orbitals to account for the interpair correlation.

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Thank you for your attention !!!