Recent developments in Natural Orbital Functional Theory: PNOF5-PT2

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The idea of a natural orbital functional (NOF) appeared few decades ago [1]. An approximate NOF requires an expression of the two-particle reduced density matrix (2-RDM) in terms of the 1-RDM. Such reconstruction of the 2-RDM has been achieved using the cumulant expansion leading to the PNOF [2]. The latter is based on an explicit ansatz of the two-electron cumulant satisfying the positivity N-representability conditions for the 2-RDM. Appropriate forms of the cumulant have led to different implementations [3], being the most successful the PNOF5 [4]. PNOF5 yields a remarkable accurate description of systems including substantial (near)degeneracy of one-particle states like diradicals [5] or transition metal dimers [6]. It has been found that the method describes correctly the dissociation limit yielding always an integer number of electrons on the dissociated atoms [7]. PNOF5 provides two complementary representations of the one-electron picture in molecules: the natural orbitals that agree closely with the empirical VSEPR theory along with the valence bond method [8], while the equivalent canonical orbitals are delocalized orbitals adapted to the symmetry of the molecule [9]. It has been recently shown that PNOF5 can be obtained as a particular case of the energy expression of an APSG wavefunction [10]. This result guarantees strictly the functional N-representability, being the PNOF5 a variational and size-consistent method, but does not account for a sufficient amount of dynamical electron correlation. To correct this problem, perturbative corrections have been implemented to the generator PNOF5-wavefunction using a multiconfiguration perturbation theory size consistent at second order (SC2-MCPT) [11,12]. Here, the theory behind the PNOF5-PT2 is outlined, and some examples are presented to illustrate the potentiality of the method. Our results are accurate values as compared to high level wave function methods and available experimental data.

Exact energy functional

$$E\left[\mathbf{\Gamma},\mathbf{D}\right]=\sum_{ik}H_{ik}\Gamma_{ki}+\sum_{ijkl}<ij|kl>D_{kl,ij}$$

Γ_{ki}: 1-RDM $D_{kl,ij}$: 2-RDM

Natural Orbital Functional

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

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

$$E\left[N,\{n_i,\phi_i\}\right]=\sum n_iH_{ii}+V_{ee}\left[N,\{n_i,\phi_i\}\right]$$

Cumulant expansion of the 2-RDM

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

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

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

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

Sum Rules: $\sum_q{}'\Delta^{\sigma\sigma}_{qp}=n_p^\sigma h_p^\sigma\ ,\quad \sum_q\Delta^{\sigma\sigma'}_{qp}=\Pi_{pp}$

N-representability

1-RDM: $0\le n_i\le 1\qquad(\sum_i\Gamma_{ii}=N)$

2-RDM: D, Q, G positive semidefinite → **Functional N-representability**

N-representability (D>0 and Q>0) $\Rightarrow\ \Delta^{\sigma\sigma'}_{qp}\le n_qn_p,\ \Delta^{\sigma\sigma'}_{qp}\le h_qh_p, q\ne p$

Total Spin Conserving Rule: $2\sum_{pq}\lambda^{\alpha\beta,\alpha\beta}_{pq,qp}=N^\beta-\sum_p n_p^\alpha n_p^\beta$

Energy Functional for Singlets

$$E^{|00\rangle}=2\sum_p n_pH_{pp}+\sum_{pq}\left(n_qn_p-\Delta_{qp}\right)\left(2J_{pq}-K_{pq}\right)+\sum_{pq}\Pi_{qp}K_{pq}$$

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

$$n_{p'}+n_p=1$$

PNOF5

$$E^{|00\rangle}=\sum_{p=1}^{N}\left[n_p\left(2H_{pp}+J_{pp}\right)-\sqrt{n_pn_{p'}}K_{pp'}\right]+\sum_{p,q=1}^{N}{}''\ n_qn_p\left(2J_{pq}-K_{pq}\right)$$

$(p'=N-p+1\,;\quad \sum'':q\ne p,p')$

Generating PNOF5-wavefunction

APSG: $|0\rangle=\prod_{p=1}^{N/2}\psi_p^\dagger|vac\rangle$, **Geminal operator:** $\psi_p^\dagger=\sqrt{n_p}a_p^\dagger a_{\bar p}^\dagger-\sqrt{n_{p'}}a_{p'}^\dagger a_{\bar p'}^\dagger$

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

$$|\Phi_0\rangle=d_0|\Psi_{HF}\rangle\,,\ d_0=\sqrt{n_1n_2\ldots n_{N/2}}\qquad\ldots$$

$$|\Phi_d\rangle=\sum_{N/2}d_p\left|\Psi^{p'\bar p'}_{p\,\bar p}\right\rangle\,,\ d_p=-d_0\sqrt{\frac{n_{p'}}{n_p}}\qquad\left|\Phi_{N/2}\right\rangle=d_{12..N/2}\left|\Psi^{1'\bar1'2'\bar2'\ldots N/2'\bar N/2'}_{1\ \bar1\ 2\ \bar2\ \ldots\ N/2\ \bar N/2}\right\rangle$$

$$|\Phi_q\rangle=\sum_{p<q}d_{pq}\left|\Psi^{p'\bar p'q'\bar q'}_{p\,\bar p\ q\,\bar q}\right\rangle,d_{pq}=d_0\sqrt{\frac{n_{p'}n_{q'}}{n_pn_q}}\qquad d_{12..N/2}=(-1)^{N/2}\sqrt{n_{1'}n_{2'}\ldots n_{N/2'}}$$

SC2-MCPT

$\{|k\rangle\}$: **Overlapping Basis** $\{\langle\tilde k|\}$: **Biorthogonal vectors**

$|0\rangle\,;\,|k\rangle\ \equiv\ |\Psi_k\rangle$: **Excited Dets.** $\langle\tilde0|=d_0^{-1}\langle\Psi_{HF}|\ ,\ k=0\,;\ \langle\tilde k|=\langle k|-d_k\langle\tilde0|,\ k>0$

$$\hat{\mathcal{H}}^0=\sum_{k=0}^{\infty}E_k|k\rangle\langle\tilde k|\ ;\qquad E_0=E^{(0)}=\langle\tilde0|\hat{\mathcal{H}}|0\rangle=\langle\Psi_{HF}|\hat{\mathcal{H}}|\Psi_{HF}\rangle-\sum_{p=1}^{N/2}\sqrt{\frac{n_{p'}}{n_p}}L_{pp'}$$

$$E_k=E_0+\Delta_k$$

$$\Delta_k=\varepsilon_r-\varepsilon_a\ ,\ \varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b\ ,\ \ldots\qquad \varepsilon_i=h_{ii}+\sum_{q=1}^{N/2}\left[2\langle iq|\,iq\rangle-\langle iq|\,qi\rangle\right]$$

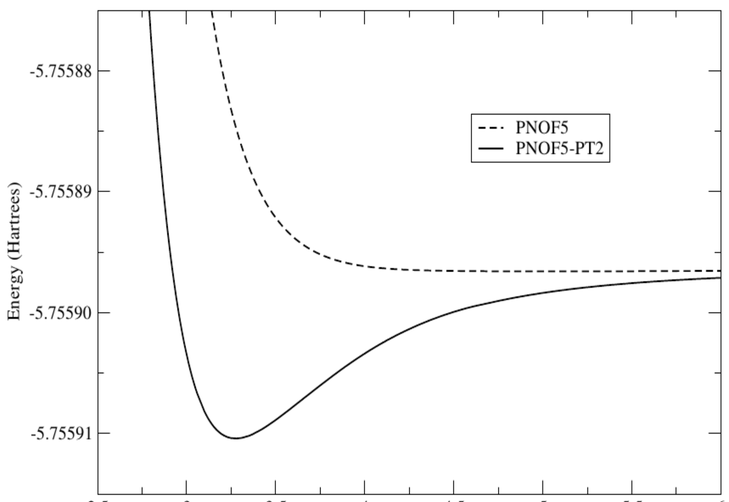
Perturbative corrections

$$E^{(1)}=\langle\tilde0|\hat{\mathcal{H}}-\hat{\mathcal{H}}^0|0\rangle=0\qquad E^{(2)}=-\sum_{k=1}^{\infty}\frac{\langle\Psi_{HF}|\hat{\mathcal{H}}|k\rangle\langle\tilde k|\hat{\mathcal{H}}|0\rangle}{d_0\Delta_k}$$

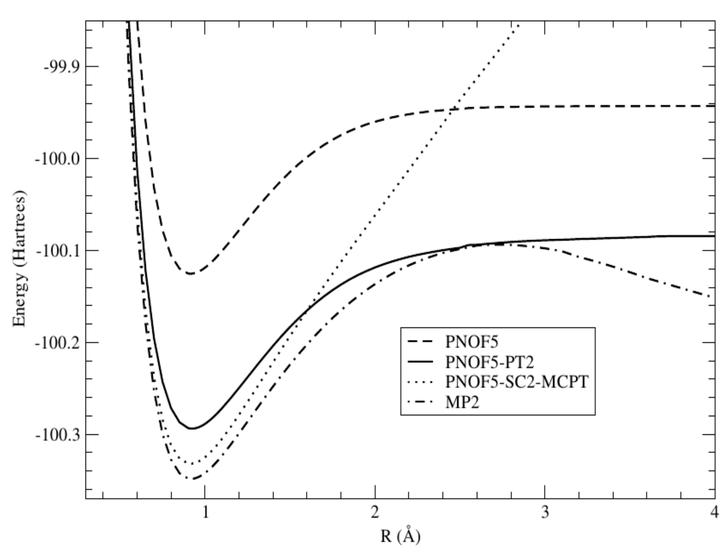
$$E^{(2)}=E^{(0)}\cdot E_c^{(2)}+E_0^{(2)}+E_d^{(2)}+E_q^{(2)}\qquad E_c^{(2)}=-\frac{1}{2}\sum_{p=1}^{N/2}\sqrt{\frac{n_{p'}}{n_p}}\frac{L_{pp'}}{(\varepsilon_{p'}-\varepsilon_p)}$$

$$E_l^{(2)}=-\sum_{k=1}^{\infty}\frac{\langle\Psi_{HF}|\hat{\mathcal{H}}|k\rangle\langle k|\hat{\mathcal{H}}|\Phi_l\rangle}{d_0\Delta_k},\ l=0,d,q\qquad L_{pp'}=\langle pp|\,p'p'\rangle$$

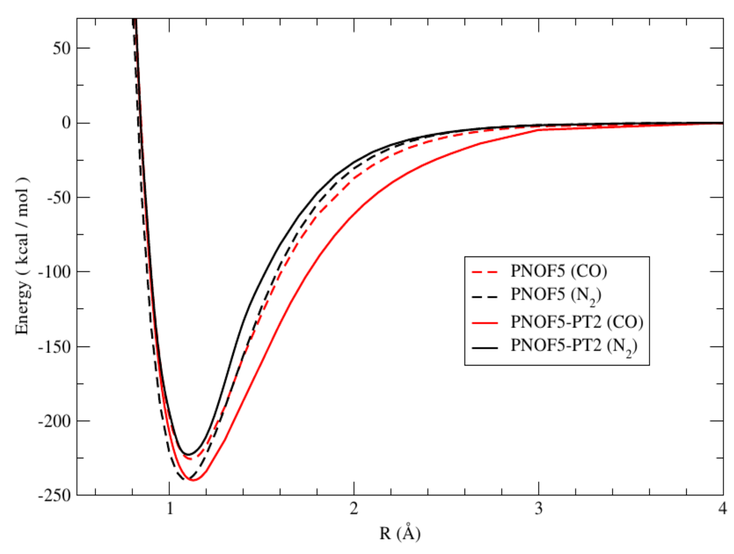
Helium Dimer (aug-cc-pV5Z)



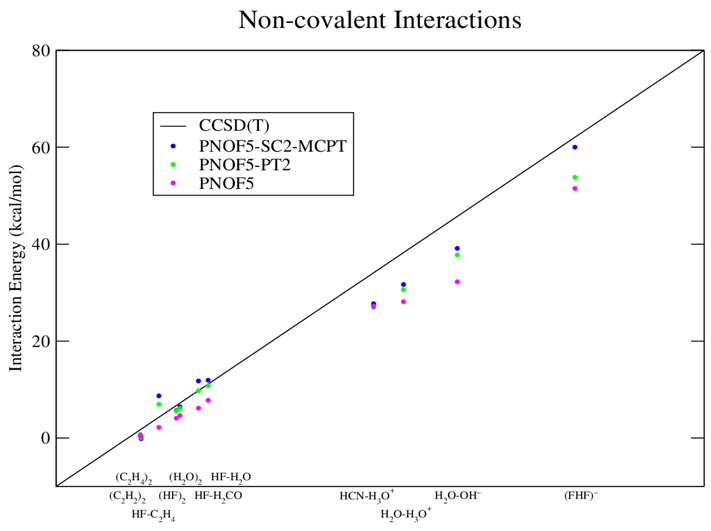
Dissociation of the FH (cc-pVTZ)



Dissociation of the CO and N_2 (cc-pVTZ)



Non-covalent Interactions



	PNOF5			PNOF5-PT2			Experimental		
Mol	R_e	ω_e	D_e	R_e	ω_e	D_e	R_{exp}	ω_e	D_e
FH	0.915	4149.3	114.5	0.924	4047.0	134.2	0.917	4138.4	141.1
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

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