Natural Orbital Functional for Multiplets

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Motivation.

- Despite its success, the Kohn-Sham density functional theory, including the spin-dependent-density formalism, can not describe the degeneracy of the spin-multiplet components.

- The proper description of the ensemble of pure spin states is provided by the one-particle reduced density matrix (1RDM) functional theory

The Goal: Achieve a method that allows to properly describe an electronic system with any value of S, but less computationally demanding than ab initio wavefunction-based methods (better scaling)

[*Phys. Rev. A 100, 032508, 2019*]

Outline

1. Introduction to the Natural Orbital Functional Theory

2. the 2RDM reconstruction for multiplets

   - PNOF7
   - PNOF7-MP2 (including missing dynamic correlation)

3. Closing Remarks

The N-electron Hamiltonian

Consider the N-electron Hamiltonian

$$\hat{H} = \sum_{ik} \mathcal{H}_{ki} \hat{a}_k^\dagger \hat{a}_i + \frac{1}{2} \sum_{ijkl} \langle kl|ij \rangle \, \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i$$

$\mathcal{H}_{ki}$: matrix elements of the one-particle part of the Hamiltonian
involving the kinetic energy and the external potential operators

$\langle kl|ij \rangle$: two-particle interaction matrix elements (Coulomb integrals)

$\hat{a}_i^\dagger$ ($\hat{a}_i$): fermion creation (annihilation) operators associated
with the complete orthonormal spin-orbital set $\{|i\rangle\}$.

- No spin coordinates $\Rightarrow \left[\hat{H}, \hat{S}^2\right] = 0, \left[\hat{H}, \hat{S}_z\right] = 0$

The exact energy functional

For a given spin S, there are $(2S + 1)$ energy degenerate eigenvectors $|SM\rangle$, so a mixed state is defined by the N-particle density matrix statistical operator:

$$\hat{\mathfrak{D}} = \sum_{M=-S}^{S} \omega_M |SM\rangle \langle SM| \qquad \left\{ \begin{array}{c} \displaystyle\sum_{M=-S}^{S} \omega_M = 1, \ \omega_M \geq 0 \\[2em] \omega_M = (2S + 1)^{-1} \end{array} \right.$$

- The energy is an explicitly functional of the 1- and 2-RDMs:

$$E\left[\mathrm{N}, \Gamma, \mathrm{D}\right] = \sum_{ik} \mathcal{H}_{ki} \Gamma_{ki} + \sum_{ijkl} \langle kl|ij \rangle D_{kl,ij}$$

$$\Gamma_{ki} = \sum_{M=-S}^{S} \omega_M \langle SM| \hat{a}_k^\dagger \hat{a}_i |SM\rangle, \quad D_{kl,ij} = \frac{1}{2} \sum_{M=-S}^{S} \omega_M \langle SM| \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i |SM\rangle$$

1RDM Functional Theory

We must only construct the 1RDM functional for the electron-electron potential:

$$V_{ee} = \sum_{ijkl} \langle kl|ij \rangle D_{kl,ij} \rightarrow V_{ee}[N,\Gamma] = \min_{D \in D(\Gamma)} \int D \, r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$$

$$E[N,\Gamma] = \mathcal{H}[N,\Gamma] + V_{ee}[N,\Gamma] \qquad (\text{Valone } 1980: \quad \hat{\mathfrak{D}}_{gs} \leftrightarrow \Gamma_{gs})$$

- Exact functionals do not have an appropriate form for computation

- $E[N,\Gamma] \equiv E[N,\Gamma,D]$ \qquad $(\hat{\mathfrak{D}}_{gs} \leftrightarrow D_{gs})$

  However, exact reconstruction has been unreachable so far

- Practical applications: $D[\Gamma] \rightarrow$ exact energy is not rebuild !

- An approximate functional still depends on the 2RDM (Donnelly 1979)

  In approximate one-particle theories, the N-representability is twofold

Ensemble N-representability

1RDM N-representability

$$\hat{\mathfrak{D}} = \sum_{M=-S}^{S} \omega_M \left| SM \right\rangle \left\langle SM \right| \Rightarrow \Gamma$$

nec. and suff. conditions:
$$0 \leq \Gamma \leq qI, \; Tr\left(\Gamma\right) = N$$

Functional N-representability

$$E\left[\mathfrak{D}\right] \equiv E\left[N, \Gamma, \overset{D\left[\Gamma\right]}{D}\right] \Rightarrow E[N, \Gamma]$$

N-representability conditions for
the reconstructed 2RDM

- *Are we really dealing with the 1RDM Functional Theory?*

  *We are no longer dealing with the 1RDMFT, but with
  approximate theories, where the 2RDM plays the dominant role*

Note: most of the approximate functionals in use are not N-representable

The ensemble N-representability conditions of the 2RDM

- There is a complete set of N-representability conditions for 2RDM: (2,q)-positivity conditions (q corresponds to the higher q-RDM). When q is the rank of the one-electron basis set, the set is complete.

  These conditions are not practical

- A complete set of N-representability conditions that do not depend on higher-order RDMs remains unknown.

- **Alternative:** use the (2,2)-positivity necessary conditions

$$\mathbf{D} \geq 0, \ \mathbf{Q} \geq 0, \ \mathbf{G} \geq 0$$

So far only the Natural Orbital Functional Theory (**NOFT**) has proven to be able to take into account functional N-representability conditions in one-particle theories, thereby from now on we focus on it.

Natural Orbitals and Occupation Numbers

The spectral decomposition of the 1-RDM:

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

$\{\phi_i\left(\mathbf{x}\right)\}$: natural spin-orbitals $\{n_i\}$: occupation numbers

- The 1-RDM in the natural orbital representation: $\Gamma_{ki} = n_i \delta_{ki}$

- Ensemble N-representable 1-RDM:

$$0 \leq n_i \leq 1, \ \sum_i n_i = \mathrm{N}$$

(necessary and sufficient conditions, Coleman 1963)

The electronic energy in NOFT

- $\mathrm{E}\left[\mathrm{N}, \{n_i, \phi_i\}\right] = \sum_i n_i \mathcal{H}_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l] < kl|ij >$

  $\mathcal{H}_{ii}$: core-Hamiltonian $\qquad < kl|ij >$: 2e- integrals

  The kinetic energy does not require the construction of a functional

- ensemble N-representable functional:

$$\mathrm{E}\left[\mathfrak{D}\right] \equiv \mathrm{E}\left[\mathrm{N}, \Gamma, D\right] \implies \mathrm{E}\left[\mathrm{N}, \{n_i, \phi_i\}\right]$$

  ensemble N-representable reconstruction

$$\hat{\mathfrak{D}} = \sum_{M=-S}^{S} \omega_M |SM\rangle \langle SM| \implies D[n_i, n_j, n_k, n_l]$$

$\hat{S}_z$ eigenfunctions

- N_I single e^- and N_{II} paired e^-: $N_I + N_{II} = N$.

- All spins corresponding to N_{II} e^- are coupled as a singlet

  $\Rightarrow$ N_I e^- determine the spin of the system

- $\hat{S}_z$ eigenfunctions θ_k are simply products of N_I 1e^- functions:

$$\theta_k = \sigma(1)\,\sigma(2)\,...\sigma(N_I)\,, \quad \sigma(i) = \left\{ \begin{array}{c} \alpha(i) \\ \beta(i) \end{array} \right.$$

$$\hat{S}_z \theta_k = \tfrac{1}{2}(\mu - \nu)\,\theta_k \quad (\mu: \text{\# of } \alpha\text{'s, } \nu: \text{\# of } \beta\text{'s})$$

- For a given μ, we have $\left(\begin{array}{c} N_I \\ \mu \end{array} \right) = \left(\begin{array}{c} N_I \\ \nu \end{array} \right)$ primitive functions

2e^-:

$\mu = 2$	$\mu = 1$	$\mu = 0$
$\alpha(1)\,\alpha(2)$	$\alpha(1)\,\beta(2)\,,\,\beta(1)\,\alpha(2)$	$\beta(1)\,\beta(2)$

Square brackets

$[\alpha^\mu \beta^\nu]$: sum of all primitive functions with μ α's and ν β's.

$$\left[\alpha^2 \beta^2\right] = \alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha + \beta\beta\alpha\alpha$$

- $[\alpha^\mu \beta^\nu]$ are simultaneous eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$:

$$\hat{S}^2 \left[\alpha^\mu \beta^\nu\right] = S\left(S+1\right)\left[\alpha^\mu \beta^\nu\right], \quad \hat{S}_z \left[\alpha^\mu \beta^\nu\right] = M\left[\alpha^\mu \beta^\nu\right]$$

$$S = N_I/2, \; M = \frac{1}{2}\left(\mu - \nu\right), \; -N_I/2 \leq M \leq N_I/2$$

- All $[\alpha^\mu \beta^\nu]$ with fixed S make up a mixed state:

$$N_I = 2, S = 1 : \quad \left\{ \begin{array}{cc} \alpha\left(1\right)\alpha\left(2\right), & M = 1 \\ \frac{1}{\sqrt{2}}\left[\alpha\left(1\right)\beta\left(2\right) + \beta\left(1\right)\alpha\left(2\right)\right], & M = 0 \\ \beta\left(1\right)\beta\left(2\right), & M = -1 \end{array} \right.$$

N_I: The mixed state of all square brackets

- It is the mixed state of highest multiplicity: $2S+1 = N_I+1$

- It is the only state with the quantum number $S = N_I/2$

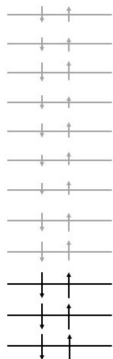- The expected value of $\hat{S}_z$ for the whole ensemble is zero:

$$<\hat{S}_z> = \sum_{M=-S}^{S} \omega_M \langle SM| \hat{S}_z |SM\rangle = \frac{1}{N_I + 1} \sum_{M=-N_I/2}^{N_I/2} M = 0$$

$\Rightarrow$ the spin-restricted theory can be adopted:

$$\phi_p^\alpha (\mathbf{r}) = \phi_p^\beta (\mathbf{r}) = \phi_p (\mathbf{r}), \; n_p^\alpha = n_p^\beta = n_p$$

The Orbital Space Ω

all spatial orbitals $\{\phi_p\}$ are double occupied in the ensemble

Weakly Occupied Orbitals

$0 \leq n_p \leq 1/2$
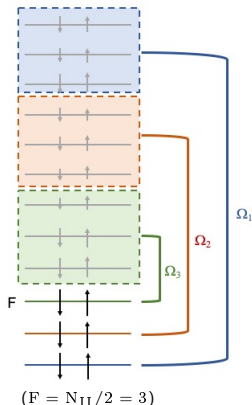
Strongly Occupied Orbitals

$1/2 \leq n_p \leq 1$

- $N = N_I + N_{II} \quad \Rightarrow \quad \Omega = \Omega_I \oplus \Omega_{II}$

  Ω_I: single electrons, Ω_{II}: paired electrons

Ω_{II} : The electron pairing restrictions

In the absence of single electrons ($N_I = 0$), the ensemble is obviously reduced to a singlet state with $N_{II}/2$ pairs.

Orbital Space $\Omega = \Omega_1 \oplus \Omega_2 \oplus \Omega_3$

Ω_1

Ω_2

Ω_3

F

($F = N_{II}/2 = 3$)

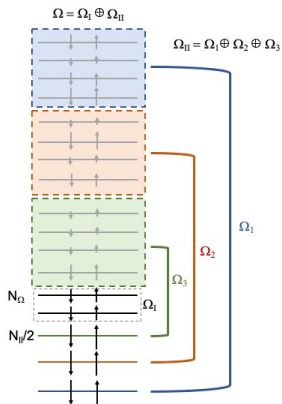$\Omega = \Omega_{II} = \Omega_1 \oplus \Omega_2 \oplus \cdots \oplus \Omega_{N_{II}/2}$

- mutually disjoint: $\Omega_{g1} \cap \Omega_{g2} = \varnothing$

- $\Omega_g \in \Omega_{II}$: 1 orbital with $g \leq N_{II}/2$,

  N_g orbitals with $p > N_{II}/2$

  $\Rightarrow \quad dim\{\Omega_g\} = 1 + N_g$

- $2 \displaystyle\sum_{q \in \Omega_g} n_q = 2 \quad (g = 1, ..., N_{II}/2)$

$\Rightarrow$ two electrons with opposite spins

Ω_I : The single occupied orbitals

$$\Omega_I = \Omega_{N_{II}/2+1} \oplus ... \oplus \Omega_{N_{II}/2+N_I}$$

- mutually disjoint: $\Omega_{g1} \cap \Omega_{g2} = \varnothing$

- $\Omega_g \in \Omega_I$: 1 orbital with $N_{II}/2 < g \leq N_\Omega$

  $\Rightarrow$ $dim\{\Omega_g\} = 1$

- $2n_g = 1 \Rightarrow n_g^\alpha = n_g^\beta = 1/2$

each orbital in Ω_I is fully occupied individually, but
we don't know whether the electron has α or β spin

Triplet : $S = 1, N_I = 2$

$(N_{II} = 6, N_g = 4, N_\Omega = N_I + N_{II}/2)$

$N = N_I + N_{II}, \ \Omega = \Omega_I \oplus \Omega_{II}$

- The splitting of the orbital space is determined by S.

  S determines the number of orbitals in Ω_I (2S)
  ($S = 1/2$: One orbital, $S = 1$: Two orbitals, and so on)

  The rest of the orbitals are distributed in Ω_{II} as a singlet
  $$dim\{\Omega_g\} = 1 + N_g, \quad N_g = (N^{orb} - N_\Omega)/N_{II}$$

- The orbitals do not remain fixed in the optimization process, they adapt to the problem. Consequently, the orbital scheme can vary along the optimization process until the most favorable orbital interactions are found.

- $2 \sum\limits_{p \in \Omega_{II}} n_p = 2 \sum\limits_{g=1}^{N_{II}/2} \sum\limits_{p \in \Omega_g} n_p = N_{II}, \quad 2 \sum\limits_{p \in \Omega_I} n_p = N_I \quad \rightarrow \quad 2 \sum\limits_{p \in \Omega} n_p = N$

2RDM reconstruction

$$\mathrm{E}\left[\mathrm{N}, \{n_i, \phi_i\}\right] = \sum_i n_i \mathcal{H}_{ii} + \sum_{ijkl} D[n_i, n_j, n_k, n_l] < kl|ij >$$

- For $\hat{S}_z$ eigenvectors: $D^{\alpha\alpha}$, $D^{\alpha\beta}$, $D^{\beta\beta}$

- satisfy (2,2)-positivity N-representability conditions

- D is divided into intra- and inter-subspace contributions

PNOF7 ($\mathcal{JKL}$-only Functional)

2RDM reconstruction: Intra-subspace contributions

- only intrapair $\alpha\beta$-contributions appear:

$$D^{\sigma\sigma}_{pq,rt} = 0, \; \sigma = \alpha, \beta$$

$$D^{\alpha\beta}_{pq,rt} = \frac{\Pi_{pr}}{2} \delta_{pq} \delta_{rt} \delta_{p\Omega_g} \delta_{r\Omega_g} \; \left(g \leq \frac{N_{\mathrm{II}}}{2} \right)$$

$$\Pi_{pr} = \left\{ \begin{array}{ll} \sqrt{n_p n_r} & p = r \text{ or } p, r > \frac{N_{\mathrm{II}}}{2} \\ -\sqrt{n_p n_r} & p = g \text{ or } r = g \end{array} \right.$$

Note: $D^{\alpha\beta}_{pp,pp} = 0, \; \forall p \in \Omega_g \in \Omega_{\mathrm{I}}$ since only $1e^-$ with α or β spin in each $|SM\rangle$.

The energy of electron pairs with opposite spins:

$$E_g = 2 \sum_{p\in\Omega_g} n_p \mathcal{H}_{pp} + \sum_{p,r\in\Omega_g} \Pi_{pr} \mathcal{L}_{pr} \quad \left(g \leq \frac{N_{\mathrm{II}}}{2} \right)$$

2RDM reconstruction: Inter-subspace contributions

inter-subspace contributions ($\Omega_f \neq \Omega_g$):

- the spin-parallel matrix elements remain Hartree-Fock like

$$D_{pq,rt}^{\sigma\sigma} = \frac{n_p n_q}{2} \left(\delta_{pr}\delta_{qt} - \delta_{pt}\delta_{qr} \right) \delta_{p\Omega_f} \delta_{q\Omega_g}, \ \sigma=\alpha,\beta$$

- the spin-antiparallel blocks are

$$D_{pq,rt}^{\alpha\beta} = \frac{n_p n_q}{2} \delta_{pr}\delta_{qt}\delta_{p\Omega_f}\delta_{q\Omega_g} - \frac{\sqrt{n_p(1-n_p)n_r(1-n_r)}}{2} \cdot$$

$$\cdot \delta_{p\Omega_f} \delta_{r\Omega_g} \left\{ \begin{array}{ll} \delta_{pq}\delta_{rt} & f \leq \frac{N_{II}}{2} \text{ or } g \leq \frac{N_{II}}{2} \\ \delta_{pt}\delta_{qr} & \frac{N_{II}}{2} < f, g \leq N_\Omega \end{array} \right.$$

Note: inter-subspace $\alpha\beta$-contributions in Ω_I lead to exchange integrals $\langle pq|qp \rangle$ instead of exchange-time-inversion $\langle pp|qq \rangle$ integrals.

PNOF7 for Multiplets

$$E = \sum_{g=1}^{N_{II}/2} E_g + \sum_{g=N_{II}/2+1}^{N_\Omega} \mathcal{H}_{gg} + \sum_{f,g=1;f\neq g}^{N_\Omega} E_{fg}$$

where

$$E_g = 2\sum_{p\in\Omega_g} n_p \mathcal{H}_{pp} + \sum_{q,p\in\Omega_g} \Pi_{qp}\mathcal{K}_{pq} \qquad (\Omega_g \in \Omega_{II})$$

$$E_{fg} = \sum_{p\in\Omega_f} \sum_{q\in\Omega_g} [n_q n_p (2\mathcal{J}_{pq} - \mathcal{K}_{pq}) - \Phi_q \Phi_p \mathcal{K}_{pq}] \qquad (\Omega_f \neq \Omega_g)$$

$$\mathcal{J}_{pq} = \langle pq|pq\rangle, \, \mathcal{K}_{pq} = \langle pq|qp\rangle, \, \Pi_{qp} = \pm\sqrt{n_q n_p}, \, \Phi_p = \sqrt{n_p(1-n_p)}$$

Note: real spatial orbitals $\rightarrow \mathcal{L}_{pq} = \mathcal{K}_{pq}$ ($\langle pp|qq\rangle = \langle pq|qp\rangle$)

Total Spin

$$<\hat{S}^2> = \frac{N(4-N)}{4} + \sum_{pq} \{D_{pq,pq}^{\alpha\alpha} + D_{pq,pq}^{\beta\beta} - 2D_{pq,qp}^{\alpha\beta}\}$$

$$\sum_{pq} \rightarrow \sum_{g=1}^{N_\Omega} \sum_{p,q\in\Omega_g} + \sum_{f\neq g=1}^{N_\Omega} \sum_{p\in\Omega_f} \sum_{q\in\Omega_g} \quad (N_\Omega = \frac{N_{II}}{2} + N_I)$$

$$\sum_{pq} D_{pq,pq}^{\sigma\sigma} = \frac{N_{II}(N_{II}-2)}{8} + \frac{N_{II}N_I}{4} + \frac{N_I(N_I-1)}{8}$$

$$\sum_{pq} D_{pq,qp}^{\alpha\beta} = \frac{N_{II}}{4} - \frac{N_I(N_I-1)}{8}$$

$$<\hat{S}^2> = \frac{N_I}{2}\left(\frac{N_I}{2}+1\right) \qquad \rightarrow \qquad S = \frac{N_I}{2}, \quad 2S+1 = N_I+1$$

Constrained Minimization of the Functional

① Pairing conditions (Löwdin's norm): $\sum_{p \in \Omega_g} n_p = 1$ $\quad (2\sum_{p \in \Omega} n_p = N)$

② N-representability of the 1-RDM: $\quad 0 \le n_p \le 1$ $\quad$ (unconstrained)

③ Orthonormality of natural orbitals: $\quad \langle \phi_p | \phi_q \rangle = \delta_{pq}$

$$\Omega = E - 2 \sum_{pq} \varepsilon_{qp} \left[<\phi_p|\phi_q> - \delta_{pq} \right] \quad \rightarrow \quad \hat{\mathcal{F}}_p |\phi_p\rangle = \sum_q \varepsilon_{qp} |\phi_q\rangle$$

$[\varepsilon, \Gamma] \ne 0 \Rightarrow$ $\quad$ solution cannot be reduced to diagonalization of ε

Self-consistent iterative diagonalization procedure based on the
Hermiticity of ε at the extremum: $\varepsilon_{pq} = \varepsilon_{qp}^*$

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

Ionization Potentials (kcal/mol) of TM Atoms (cc-pVTZ)

Atom	X	X^+	PNOF7	CCSD(T)	EXP
Sc	^{2}D	^{3}D	143.8	146.8	151.3
Ti	^{3}F	^{4}F	151.7	152.8	157.5
V	^{4}F	^{5}D	151.1	149.4	155.2
Cr	^{7}S	^{6}S	141.8	147.9	156.0
Mn	^{6}S	^{7}S	167.1	166.0	171.4
Fe	^{5}D	^{6}D	183.1	176.2	182.3
Co	^{4}F	^{3}F	182.8	173.3	181.5
Ni	^{3}F	^{2}D	187.8	164.5	175.1
Cu	^{2}S	^{1}S	178.9	167.0	178.2
Zn	^{1}S	^{2}S	189.0	208.0	216.6
MAE			7.9	7.3	

Ionization Potentials of Transition Metal Atoms Sc-Zn
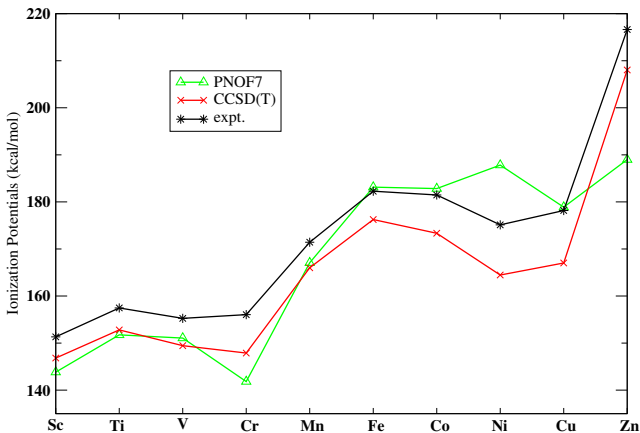
NOF-MP2: Global Method for Electron Correlation

- Weakness of PNOF7: Inter-subspace dynamic correlation

  $$\Phi_p = \sqrt{n_p(1 - n_p)} \approx 0 \text{ for ONs close to 1 and 0}$$

  $\Rightarrow$ complete intra-subspace, but only static inter-subspace

- To add the missing dynamic correlation: NOF-MP2

  1. Phys. Rev. Lett. 119, 063002 (2017); arXiv:1708.03719

  2. Phys. Rev. A 98, 022504 (2018); arXiv:1808.06070.

  PNOF7 provides the reference NOs to form $\tilde{E}_{hf}$:

  $$\tilde{E}_{hf} = E^{(0)} + E^{(1)} = 2 \sum_{g=1}^{N_\Omega} \mathcal{H}_{gg} + \sum_{f,g=1}^{N_\Omega} (2\mathcal{J}_{fg} - \mathcal{K}_{fg}) - \sum_{g=\frac{N_\Pi}{2}+1}^{N_\Omega} \frac{\mathcal{J}_{gg}}{4}$$

  closed-shell-like Fockian with doubly ($2n_g = 2$) and singly ($2n_g = 1$) occupied orbitals.

NOF-MP2: Global Method for Electron Correlation

$$
\text{MP2:} \left\{ \begin{array}{l} \hat{H}^{(0)} = \sum_{ik} \mathcal{F}_{ki} \hat{a}_k^\dagger \hat{a}_i, \ \hat{V} = \hat{H} - \hat{H}^{(0)} \\[2ex] \left| \Psi^{(0)} \right\rangle = |\phi_1 \ldots \phi_i \ldots \phi_N\rangle \ \text{(Slater)} \\[2ex] \left| \Psi^{(1)} \right\rangle = \frac{1}{2} \sum_{ijab} T_{ab}^{ij} \left| \Psi_{ij}^{ab} \right\rangle \end{array} \right\} \rightarrow \quad E = \tilde{E}_{hf} + E^{(2)}
$$

$$
E^{(2)} = \sum_{g,f=1}^{N_\Omega} \sum_{p,q>N_\Omega}^{M} A_g A_f \langle gf | pq \rangle \left[2 T_{pq}^{gf} - T_{pq}^{fg} \right], \ A_g = \left\{ \begin{array}{ll} 1 & 1 \le g \le N_{II}/2 \\ 1/2 & N_{II}/2 < g \le N_\Omega \end{array} \right.
$$

$$
\langle ab | ij \rangle + \sum_c \left(\mathcal{F}_{ac} T_{cb}^{ij} + T_{ac}^{ij} \mathcal{F}_{cb} \right) - \sum_k \left(\mathcal{F}_{ik} T_{ab}^{kj} + T_{ab}^{ik} \mathcal{F}_{kj} \right) = 0
$$

$$
\Rightarrow \quad E = \tilde{E}_{hf} + E_{PNOF7}(\Pi, \Phi) + E^{(2)}
$$

Avoiding the double counting

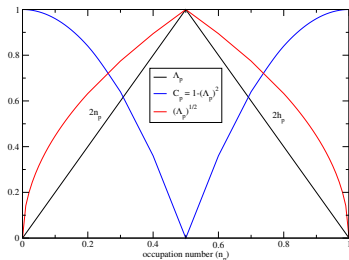$$E^{sta} = \sum_{g=1}^{N_\Omega} E_g^{sta} + \sum_{f \neq g}^{N_\Omega} E_{fg}^{sta} \qquad E^{dyn} = \sum_{g=1}^{N_\Omega} E_g^{dyn} + \sum_{f \neq g}^{N_\Omega} E_{fg}^{dyn}$$

intra: $\quad \sqrt{\Lambda_p} = \begin{cases} \sqrt{2h_p}, & p \leq N_\Omega \\ \sqrt{2n_p}, & p > N_\Omega \end{cases} \qquad C_p^{tra} = 1 - \Lambda_p^2$

inter: $\quad \Theta_p = 2\sqrt{n_p h_p} \qquad\qquad C_p^{ter} = 1 - \Theta_p^2$

Avoiding the double counting

$$E_{intra}^{sta} = \sum_{g=1}^{N_{II}/2} E_g^{sta} = \sum_{g=1}^{N_{II}/2} \sum_{q,p \in \Omega_g, q \neq p} \sqrt{\Lambda_q \Lambda_p} \, \Pi_{qp} \, \mathcal{K}_{pq}$$

$$E_{inter}^{sta} = \sum_{f,g=1; f \neq g}^{N_\Omega} E_{fg}^{sta} = -\sum_{f \neq g}^{N_\Omega} \sum_{p \in \Omega_f} \sum_{q \in \Omega_g} \Theta_q \Phi_q \Theta_p \Phi_p \mathcal{K}_{pq}$$
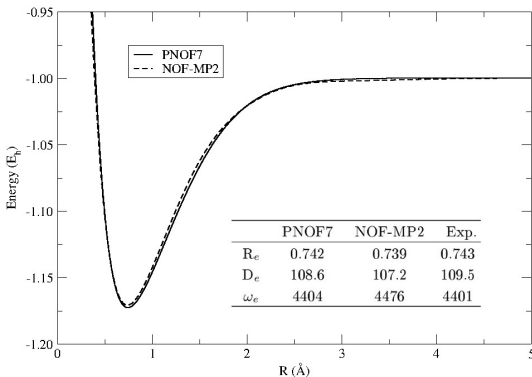
$$\tilde{\mathcal{F}}_{pq} = C_p^l C_q^l \mathcal{F}_{pq}, \quad \widetilde{\langle pq| \, rt \rangle} = C_p^l C_q^l C_r^l C_t^l \langle pq| \, rt \rangle \qquad (l = tra, \, ter)$$

$$\left. \begin{array}{l} \widetilde{\langle ab| \, ij \rangle} + \left(\mathcal{F}_{aa} + \mathcal{F}_{bb} - \mathcal{F}_{ii} - \mathcal{F}_{jj} \right) T_{ab}^{ij} + \sum_{c \neq a} \tilde{\mathcal{F}}_{ac} T_{cb}^{ij} \\ + \sum_{c \neq b} T_{ac}^{ij} \tilde{\mathcal{F}}_{cb} - \sum_{k \neq i} \tilde{\mathcal{F}}_{ik} T_{ab}^{kj} - \sum_{k \neq j} T_{ab}^{ik} \tilde{\mathcal{F}}_{kj} = 0 \end{array} \right\} \Rightarrow \quad E_{MP2}^{dyn} = E^{(2)}$$

$$E = \tilde{E}_{hf} + E_{PNOF7}^{sta} + E_{MP2}^{dyn}$$

Intra-pair electron correlation

Potential energy curves for H_2 / cc-pVTZ :

	PNOF7	NOF-MP2	Exp.
R_e	0.742	0.739	0.743
D_e	108.6	107.2	109.5
ω_e	4404	4476	4401

Phys. Rev. Lett. 119, 063002 (2017)

Ionization Potentials (kcal/mol) of TM Atoms (cc-pVTZ)

Atom	X	X^+	PNOF7	CCSD(T)	PNOF7-MP2	EXP
Sc	^{2}D	^{3}D	143.8	146.8	148.4	151.3
Ti	^{3}F	^{4}F	151.7	152.8	156.7	157.5
V	^{4}F	^{5}D	151.1	149.4	149.2	155.2
Cr	^{7}S	^{6}S	141.8	147.9	160.7	156.0
Mn	^{6}S	^{7}S	167.1	166.0	174.4	171.4
Fe	^{5}D	^{6}D	183.1	176.2	177.5	182.3
Co	^{4}F	^{3}F	182.8	173.3	165.7	181.5
Ni	^{3}F	^{2}D	187.8	164.5	166.7	175.1
Cu	^{2}S	^{1}S	178.9	167.0	167.6	178.2
Zn	^{1}S	^{2}S	189.0	208.0	208.3	216.6
MAE			7.9	7.3	6.5	

Ionization Potentials of Transition Metal Atoms Sc-Zn
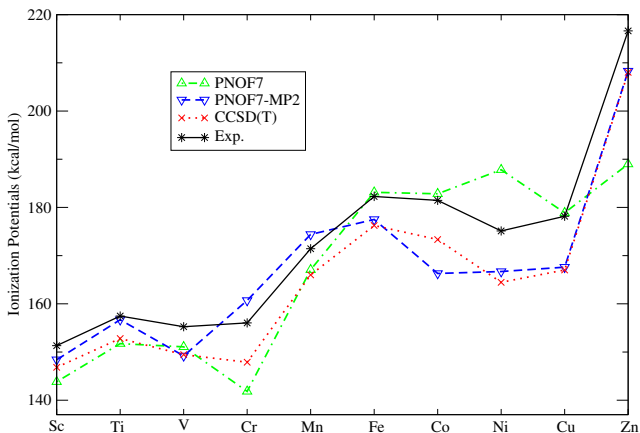
Closing remarks

- New natural orbital functional for multiplets
  - Functional N-representability: $\mathfrak{D} \Rightarrow D[n_i, n_j, n_k, n_l]$
  - PNOF7 for singlets has been extended to multiplets
  - PNOF7 seems to recover the whole static correlation

- PNOF7-MP2:
  - single-reference method
  - static and dynamic electron correlations in one shot
  - TM atoms Sc-Zn Ionization Potentials

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Thank you for your attention !!!