The FLOSIC Route to Self-interaction-free DFT

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- Standard density functionals have the form:

$$E^{DFT}[n] = T_s + E_{ext}[n] + E_{Coul}[n] + E_{xc}[n_\uparrow, n_\downarrow]$$

$$\underbrace{\phantom{E_{ext}[n] + E_{Coul}[n]}}_{\text{known}} \quad \underbrace{\phantom{E_{xc}[n_\uparrow, n_\downarrow]}}_{\text{unknown}}$$

- For a **one-electron** density n_i, the exact (unknown) functional should satisfy

$$E_{Coul}[n_i] = -E_{xc}[n_i, 0]$$

so that $E_{Coul} + E_{xc}$ cancel out **exactly** and there is no "self-interaction"

- Approximate density functionals **do not** satisfy this

What is self-interaction in DFT?

- This produces a residual, unphysical self-interaction of the electrons

- In other words, electrons "see" themselves, while they should not

- While modern functionals can be very accurate for describing many properties in many cases, self-interaction errors (SIE) still cause problems…and it is embarrassing

Self-interaction error leads to:

- Incorrect asymptotic behavior
- Unphysical delocalization of charge
- Many other problems

Accuracy improves, more exact conditions are satisfied

Etc.
Rung 4: Explicit occupied orbital dependent (hybrids, etc.)
Rung 3: Meta-Generalized Gradient Approximation
Rung 2: Generalized Gradient Approximation (GGA)

Rung 1: Local Density Approximation (LDA)

Self-interaction is still present!

Perdew-Zunger self-interaction correction (PZ-SIC)

- Orbital-by-orbital removal of self-interaction

- $E^{DFT-SIC} = E^{DFT} + \sum_{i=1}^{N} U^{SIC}[n_i]$ $\qquad$ $U^{SIC}[n_i] = -E_{Coul}[n_i] - E_{xc}[n_i]$

- SIC equations:

$$\{H_{o\sigma} + V_{i\sigma}^{SIC}\}\phi_{i\sigma} = H_{i\sigma}\phi_{i\sigma} = \sum_{j=1}^{N_{occ}} \lambda_{ji}^{\sigma}\phi_{j\sigma} \qquad (n_i = |\phi_i|^2)$$

- Localization equations (traditional PZ-SIC) - conditions for minimum energy

$$\langle \phi_{i\sigma}|V_{i\sigma}^{SIC} - V_{j\sigma}^{SIC}|\phi_{j\sigma}\rangle = \lambda_{ji}^{\sigma} - \lambda_{ij}^{\sigma} = 0$$

- Orbital density dependent

Why isn't PZ-SIC more widely used?

- Particular choice of **local** orbitals minimizes energy

- Computationally challenging:
  - Determine occupied space **plus** a **unitary transformation** to localize orbitals
  - Energy is not invariant under rotation of orbitals
  - M(M-1)/2 conditions (on top of DFT)
  - Multiple evaluations of $U^{SIC}[n_i]$

- It adds an extra burden that scales as M^2

Pederson *et al.*, JCP 86, 2688 (1985)
Vydrov & Scuseria, JCP 121, 8187 (2004)
Lethola & Jónsson, JCTC 10, 5324 (2014)

What do we know about SIC so far?

(since 1981)

- SIC-DFT **improves** thermochemistry of molecules **only** for LDA

- SIC correction **disrupts** the physical constraints built into GGAs, meta-GGAs, and hybrids

- For many properties little is known

- It is computationally expensive

- **DFU+U** and **hybrid** functionals are perhaps the best reference of what to expect for explicitly self-interaction free DFT

- General consensus was 'it is not worth the trouble'

Paradox of SIC: How can anything so right be so wrong? Perdew et al. Adv. in Atomic, Mol, Opt. Phys. 64 (2015)

Calculated formation enthalpies (kcal/mol) for G2 test set

TABLE II. Deviations from experiment of standard enthalpies of formation ($\Delta_f H^\circ_{298}$) for the G2-1 test set computed with self-interaction-corrected and self-interaction-uncorrected functionals using the 6-311 +G($3df,2p$) basis set. The geometries and zero-point energies were obtained at the B3LYP/6-31G($2df,p$) level using a frequency scale factor of 0.9854. All values are in kcal/mol.

Functional	ME	MAE	Max (+)	Max (−)
DFT				
SVWN5	−36.0	36.1	0.5 (Li_2)	−86.1 (CO_2)
PBE	−6.6	8.1	10.7 (Si_2H_6)	−28.9 (CO_2)
PBE0	1.4	2.9	9.8 (SiO)	−5.9 (BeH)
BLYP	−2.8	4.8	10.7 (Si_2H_6)	−15.4 (O_2)
B3LYP	−0.4	2.2	7.6 (SO_2)	−8.0 (BeH)
VSXC	−0.4	2.3	8.0 (N_2H_4)	−7.5 (O_2)
TPSS	−3.6	4.5	5.6 (SiO)	−18.1 (Si_2H_6)
SIC				
PZ-SVWN5	−21.5	22.8	8.4 (SiO)	−89.2 (C_2H_6)
PZ-PBE	10.0	12.5	63.6 (CO_2)	−11.5 (PH_2)
PZ-PBE0	13.6	14.9	63.5 (CO_2)	−7.7 (PH_2)
PZ-BLYP	18.6	21.0	99.7 (CO_2)	−13.9 (PH_2)
PZ-B3LYP	15.7	18.7	86.0 (CO_2)	−13.6 (Si_2H_6)
PZ-VSXC	13.6	16.5	69.4 (CO_2)	−24.7 (Si_2H_6)
PZ-TPSS	15.0	19.5	83.9 (CO_2)	−27.9 (Si_2H_6)

- Results for LDA improved but any other functional worsens
- No significant improvement over standard DFT

Vydrov & Scuseria, J. Chem. Phys. 121, 8187 (2004)

The FLOSIC route to self-interaction free DFT

For a given set of ψ_α orthonormal orbitals:

- Fermi-Löwdin orbitals: $\quad F_i(\mathbf{r}) = \dfrac{\sum_\alpha \psi_\alpha^*(\boldsymbol{a}_i)\psi_\alpha(\mathbf{r})}{\sqrt{n(\boldsymbol{a}_i)}} \qquad n(\boldsymbol{a}_i) = \sum_\alpha |\psi_\alpha(\boldsymbol{a}_i)|^2$

- These Fermi orbitals $F_i(\mathbf{r})$ are normalized but not orthonormal
- Orthogonalization: Löwdin
- One localized orbital for each descriptor $\boldsymbol{a}_i$ (FOD)
- Replaces the unitary transformation from MOs→ LOs by $\{\boldsymbol{a}_i\}$

- Still need to minimize the energy with respect to occupied space and $\boldsymbol{a}_i$
- FLOSIC: Fermi-Löwdin Self-Interaction Correction

Pederson, Ruzsinszky, Perdew, J. Chem. Phys. 140, 121103 (2014)

- Effectively removes SIE
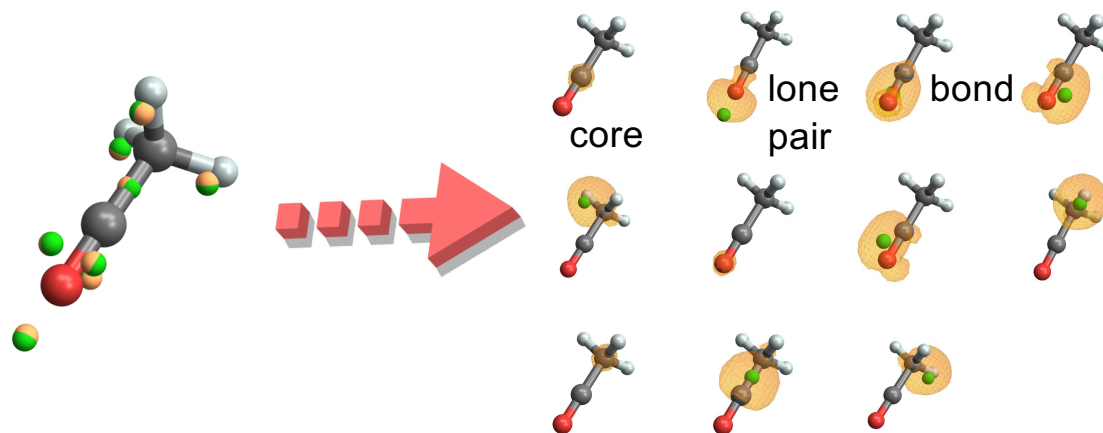- Computationally more expensive than DFT, but scales better than previous SIC methods

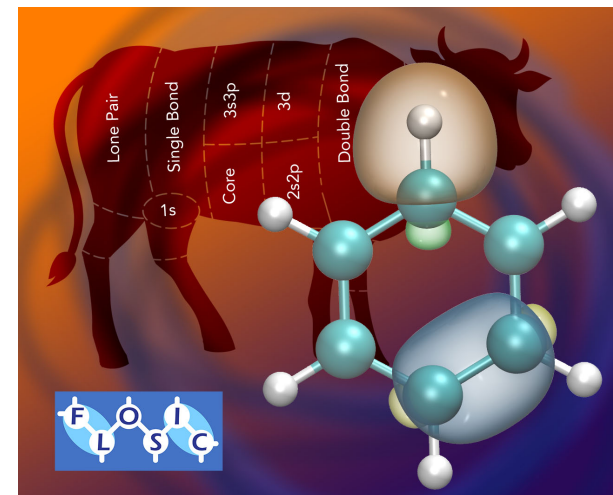| **DFT**	**Traditional PZ**	**FLOSIC**
$E(\mathbb{P})$	$E(\mathbb{P}, \mathbb{U})$	$E(\mathbb{P}, \mathbb{a})$
	$+N(N-1)/2$	$+3N$

- Fermi orbital descriptors contain chemical information

core lone pair bond

The FLOSIC route to self-interaction free DFT
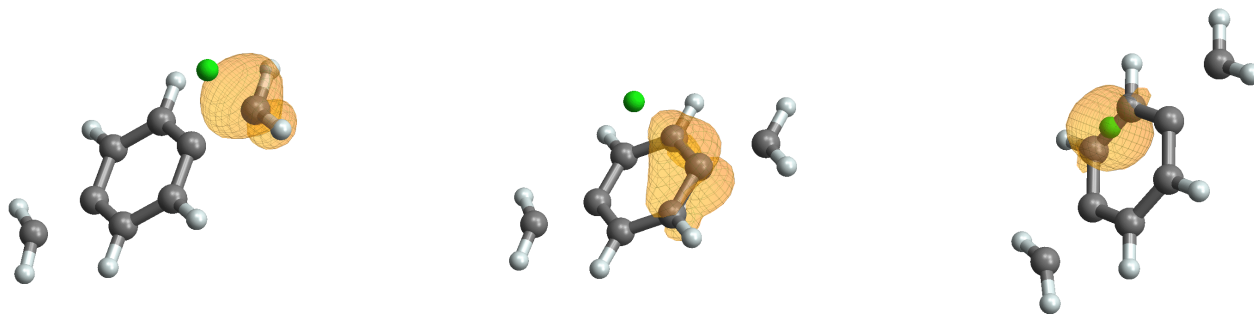
- One localized orbital per descriptor a_i
- FLOs are orthonormal
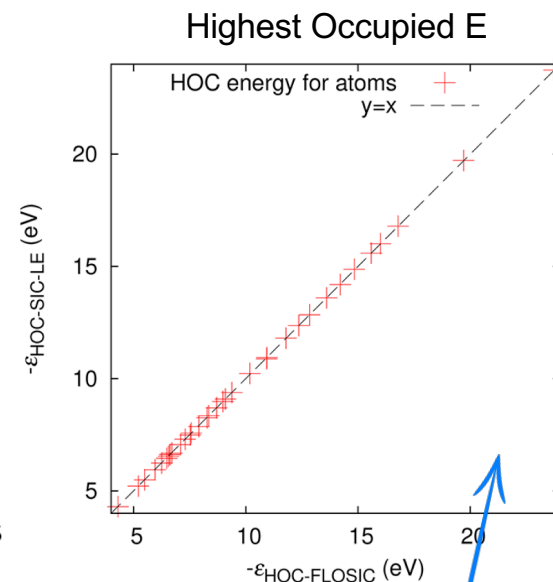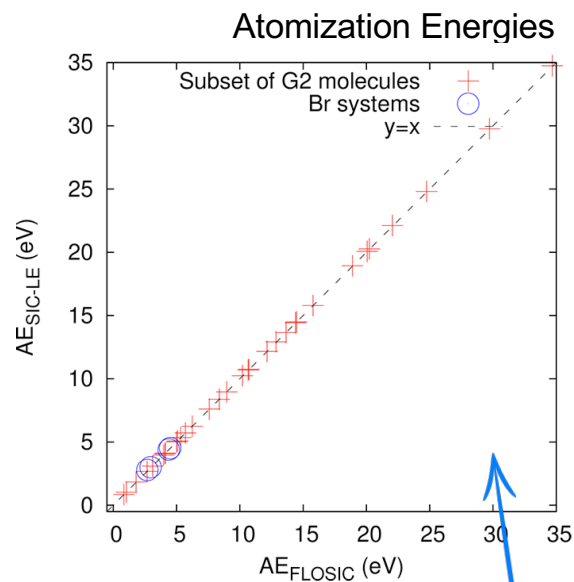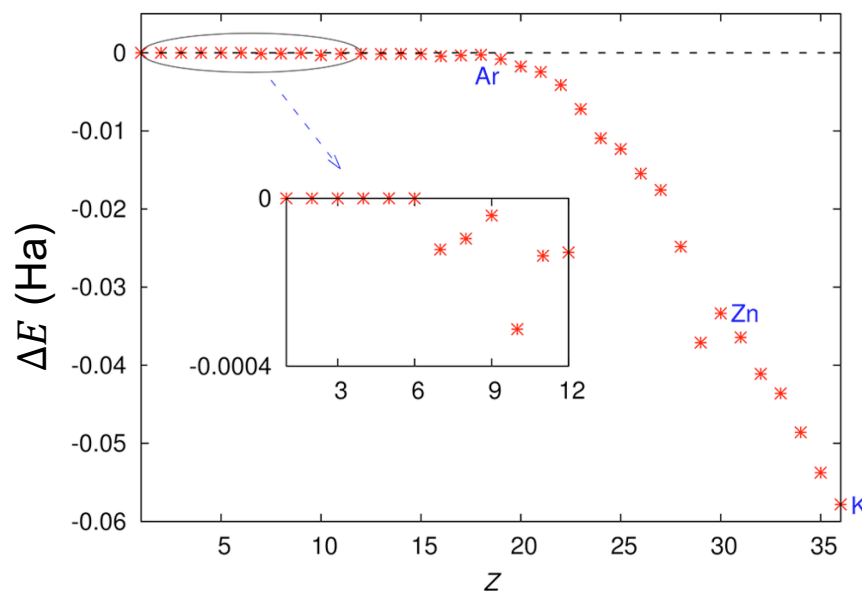- In many cases initial FODs are easy to predict

The FLOSIC route to self-interaction free DFT

Structure of the code (under development)

```
┌──────────────────┐
│ Initial density  │ ─ ─ ─ ─ ─ ─ ─ ─→  ┌──────────────────┐      How to get "good" initial FODs?
│   and FODs       │                   │  FOD generators  │
└──────────────────┘                   └──────────────────┘
        │
        ▼
┌──────────────────┐                   ┌──────────────────┐      How to minimize the evaluation
│ Find optimal     │ ─ ─ ─ ─ ─ ─ ─ ─→  │ 2-SCF approach,  │      of $V_{i\sigma}^{SIC}$?
│ density (SCF)    │                   │ Unified          │
└──────────────────┘                   │ Hamiltonian      │
        │                              └──────────────────┘
        ▼
┌──────────────────┐
│ Calculate FOD    │
│ gradients        │
└──────────────────┘
        │
        ▼
    ╱‾‾‾‾‾╲         no    ┌──────────┐
   ╱ Small ╲ ─────────→  │ New FODs │ ─ ─ ─ ─ ─→  ┌──────────────────────────┐   How to relax FODs faster?
   ╲ FOD    ╱            └──────────┘             │ • LBFGS, GDIIS, etc.     │
    ╲grad? ╱                                      │ • ECPs, Freezing, etc.   │
     ╲___╱                                        └──────────────────────────┘
      │
     yes
      │
      ▼
 ┌────────┐
 │  Done  │
 └────────┘
```
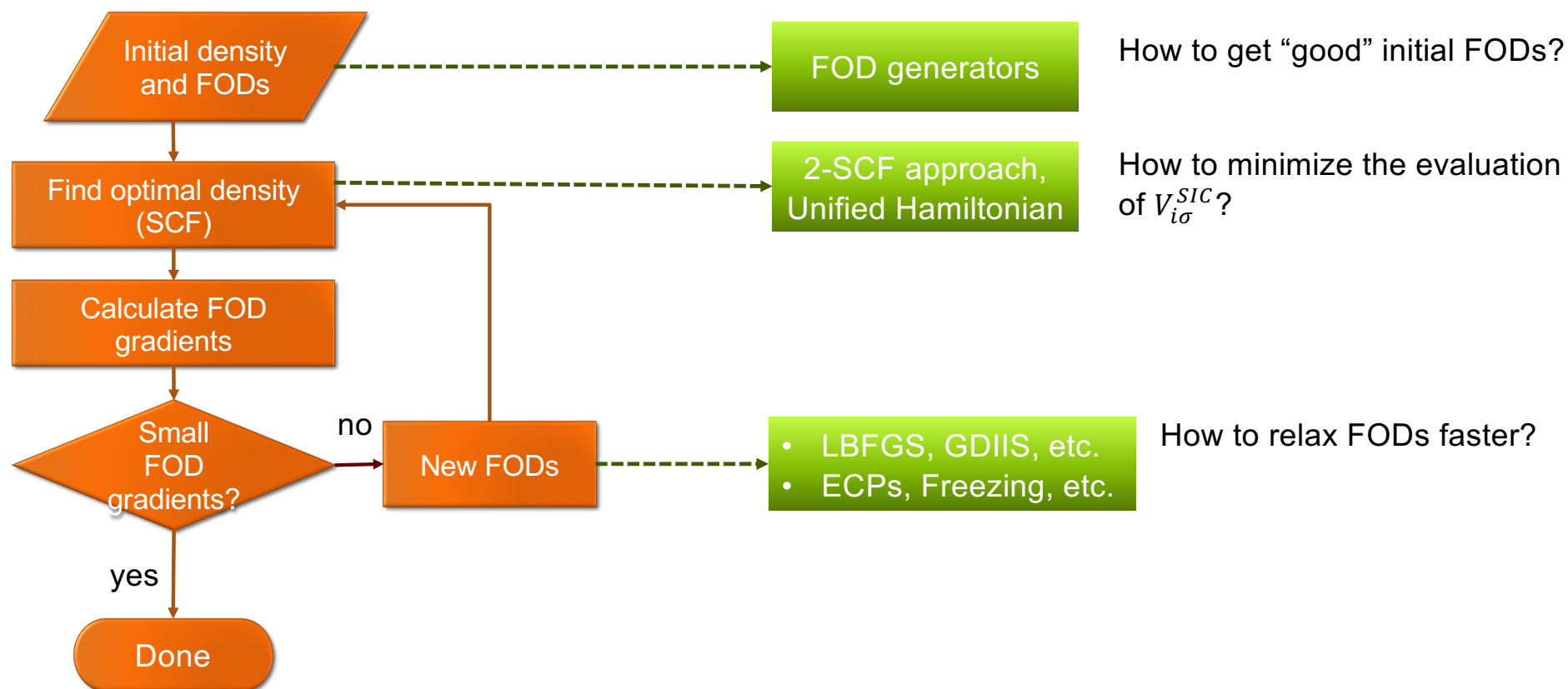
Atomic gradients also available: JCC 40, 820 (2019)

Atomization Energies

Highest Occupied E

- Total FLOSIC energy above PZ-SIC
- Most of the difference in ΔE comes from the 1s
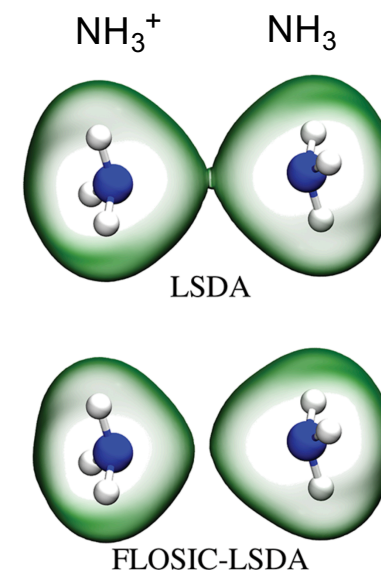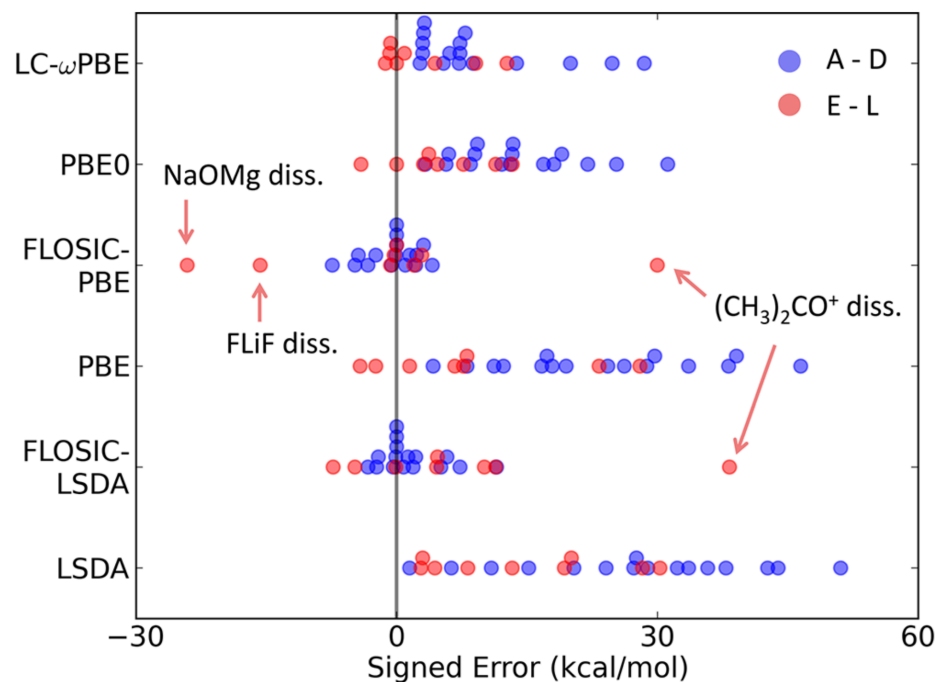- 1s contributions to AE cancel out

Physical properties identical

Whithanage et al., JCTC 14, 4122 (2018)
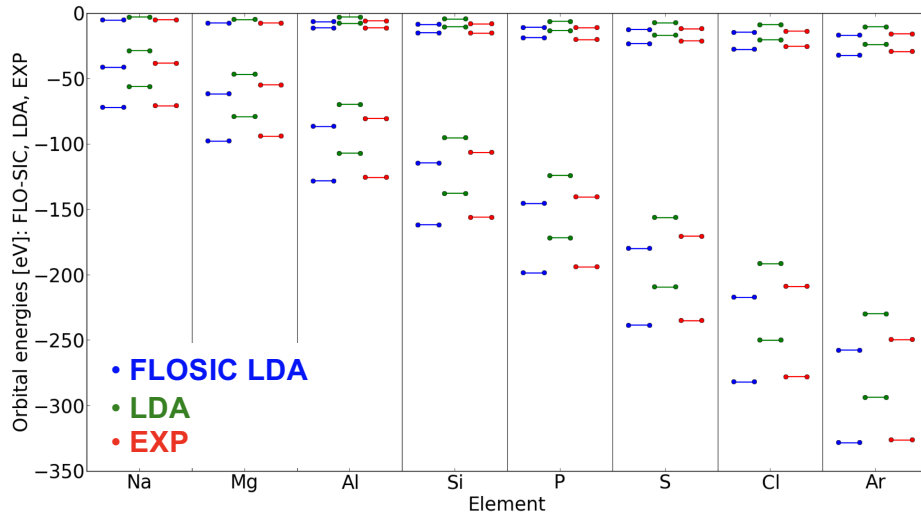
SIE4x4 and SIE11 test sets (from Grimme)

	reaction
A	$H_2^+ \rightarrow H + H^+$
B	$He_2^+ \rightarrow He + He^+$
C	$(NH_3)_2^+ \rightarrow NH_3 + NH_3^+$
D	$(H_2O)_2^+ \rightarrow H_2O + H_2O^+$
E	$C_4H_{10}^+ \rightarrow C_2H_5 + C_2H_5^+$
F	$(CH_3)_2CO^+ \rightarrow CH_3 + CH_3CO^+$
G	$ClFCl \rightarrow ClClF$
H	$C_2H_4 \cdots F_2 \rightarrow C_2H_4 + F_2$
I	$C_6H_6 \cdots Li \rightarrow Li + C_6H_6$
J	$NH_3 \cdots ClF \rightarrow NH_3 + ClF$
K	$NaOMg \rightarrow MgO + Na$
L	$FLiF \rightarrow Li + F_2$

- Improved errors when SIC is important
- Less statistical dispersion than DFT

Sharkas et al., JPCA 122, 9307 (2018)

Highlights: Orbital Energies

Atomic orbital energies for 2s2p and 3s3p shells

- FLOSIC LDA
- LDA
- EXP

DOS of ZnO from: Schmidt and Kümmel, Computation 2016, 4, 33

→ Standard DFT

→ Hybrid functionals: partially counteract the SIE

→ Self-interaction free calculation
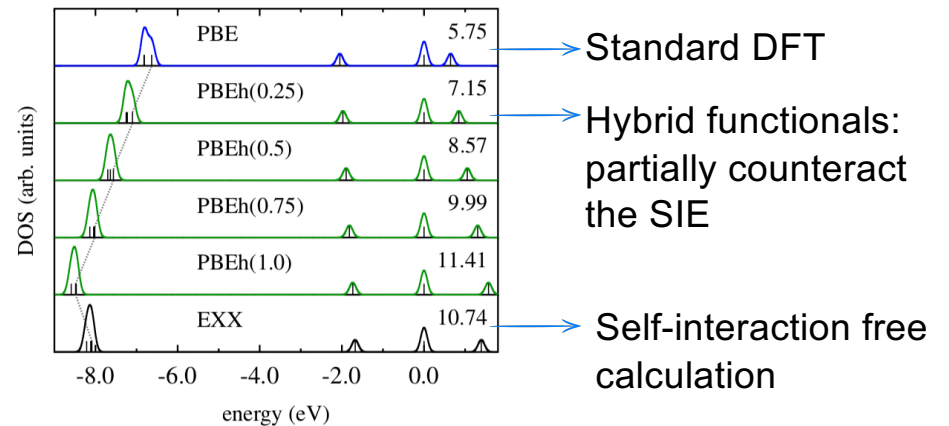
- FLO-SIC orbital energies improved for core *and* valence levels
- Better approximations of removal energies
- Differential localization of *s,p,d* orbitals

Jackson et al., J. Phys. Conf. Ser. (in press, 2019)

Highlights: Magnetic Exchange Couplings

"Toy" system (4 e) that allows us to compare with very accurate wave function calculations
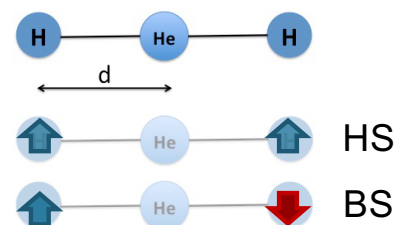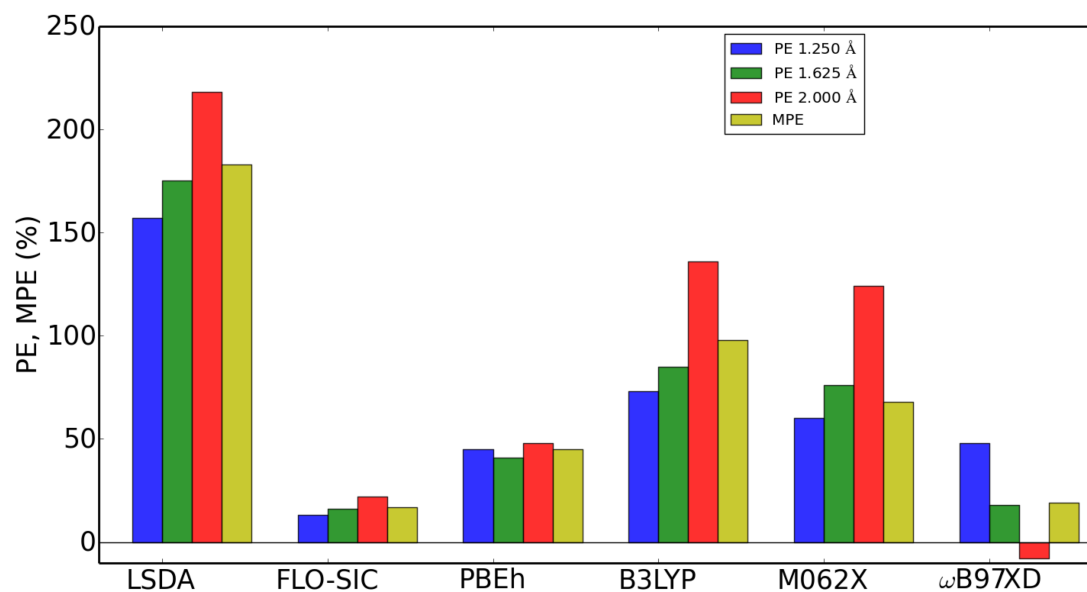
d (Å)	1.250	1.625	2.000
LSDA	-12493	-1494	-159
FLO-SIC	-5503	-632	-61
PBEh	-7041	-766	-74
B3LYP	-8415	-1007	-118
M06-2X	-7755	-958	-112
ωB97XD	-7174	-643	-46
PZ-SIC *	-5414	-614	-62
Full-CI *	-4860	-544	-50

* From Ruiz et al. JCP 123, 164110 (2005)
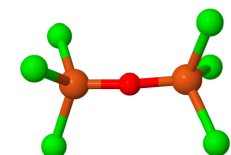
Joshi et al., JCP 149, 164101 (2018)

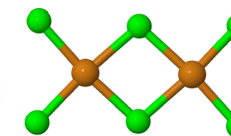## Highlights: Magnetic Exchange Couplings

FLOSIC calculations

- Effective core potentials (10 core electrons)
- Fully optimized FOD and orbitals
- Time consuming calculations

Method	$[Cu_2Cl_6]^{2-}$	$[Fe_2OCl_6]^{2-}$
LSDA	-493	-495
FLOSIC-LSDA	-201	-97
PBEh	-31	-377
B3LYP	-56	-443
M06-2X	23	-284
wB97XD	47	-384
Experiment	0 to -40	-112

J couplings in cm^{-1}

$[Fe_2OCl_6]^{2-}$

$[Cu_2Cl_6]^{2-}$

- FLOSIC reduces the AF interaction – same as hybrids

Joshi et al., JCP 149, 164101 (2018)

Summary

- SIC improves DFT in many aspects but harms "bonding" thermochemistry
- FLOSIC opens the possibility for practical **self-interaction free** DFT
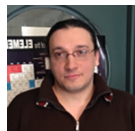- Need to combine **efficient** SIC algorithms with **SIC-friendly** DFT realizations

Fermi
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Orbital
Self
Interaction
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www.flosic.org

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