

Fermi-Löwdin orbitals for SIC

Recovering chemical concepts / improved correlation energies

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Self interaction-correction with Fermi-Löwdin orbitals

The self-interaction error

$$E_H = \frac{1}{8\pi\epsilon} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- E_H should be zero for single electron
→ but it is not !
- Perdew, Zunger (1981):

$$E_{XC}^{PZ-SIC} = - \sum_{i,\sigma} \{U[\rho_{i,\sigma}] + E_{XC}^{approx}[\rho_{i,\sigma}, 0]\}$$

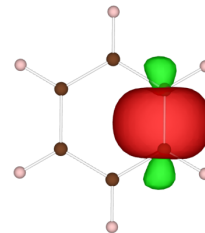
$$\{H_{0,\sigma} + V_{i,\sigma}^{SIC}\} |\psi_{i,\sigma}\rangle = \sum_j \lambda_{ij}^\sigma |\psi_{j,\sigma}\rangle$$

- Orbital dependent functional leads to excessive computational demands

Perdew, J. P., Zunger, A., *Phys. Rev. B*, 23 5048 (1981).

Fermi-Löwdin orbital SIC

$$F_{i\sigma}(\mathbf{r}) = \frac{\sum_{\alpha} \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r})}{\sqrt{\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2}}$$



1. Transform KS-orbitals Ψ to Fermi-orbitals F_i
2. Use Löwdin-orthogonalization $F_i \rightarrow \phi_i$

$$\sum_j S_{ij} T_{\alpha j} = Q_{\alpha} T_{\alpha i} \rightarrow |\phi_k\rangle = \sum_{\alpha j} \frac{1}{\sqrt{Q}} T_{\alpha k} T_{\alpha j} |F_j\rangle$$

3. Minimization of total energy incl. E_{SIC}
(finding 3N reference positions \mathbf{a}_i)

Pederson, M. R. et al., *J. Chem. Phys.* 140, 121103 (2014).

Pederson, M. R., *J. Chem. Phys.*, 142, 064112 (2015).

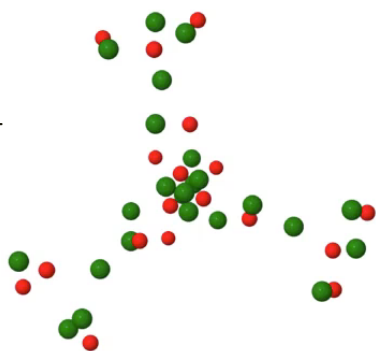
Density Functional Theory + FLO-SIC

$$F_{i\sigma}(\mathbf{r}) = \frac{\sum_{\alpha} \psi_{\alpha\sigma}^* \mathbf{a}_{i\sigma} \psi_{\alpha\sigma}(\mathbf{r})}{\sqrt{\sum_{\alpha} |\psi_{\alpha\sigma} \mathbf{a}_{i\sigma}|^2}}$$

Gradients of FLO

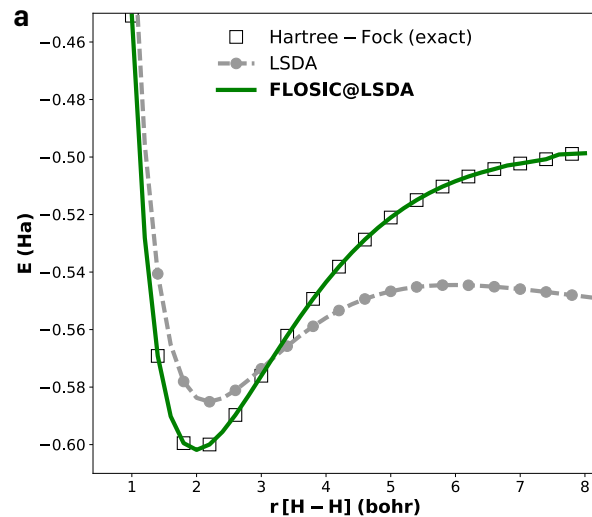
$$\frac{dE^{SIC}}{d\mathbf{a}_i} = \sum_k \left(\left\langle \frac{d\phi_k}{d\mathbf{a}_i} \middle| V_k^{SIC} \middle| \phi_k \right\rangle + \left\langle \phi_k \middle| V_k^{SIC} \middle| \frac{d\phi_k}{d\mathbf{a}_i} \right\rangle \right), E_{tot} \rightarrow \min$$

SO₄²⁻

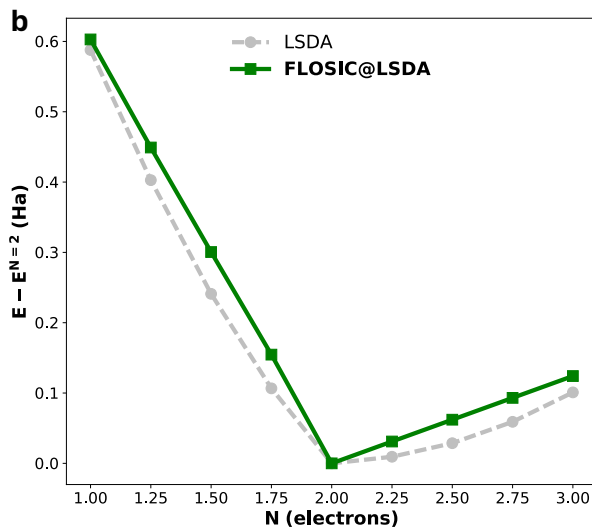


Jmol

- Reference positions (descriptors) of the Fermi orbitals
- Optimized to find minimal total energy (including the SIC energy)



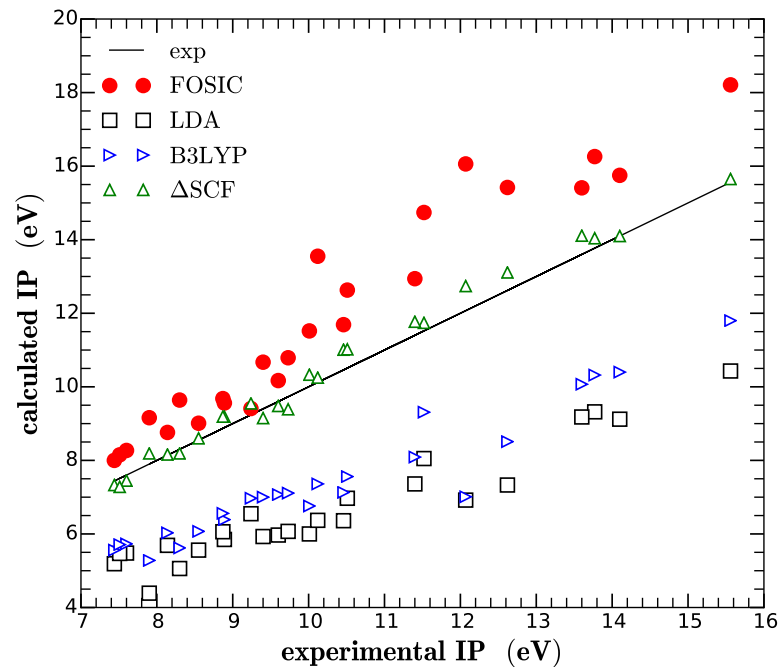
H₂⁺ Binding Energy



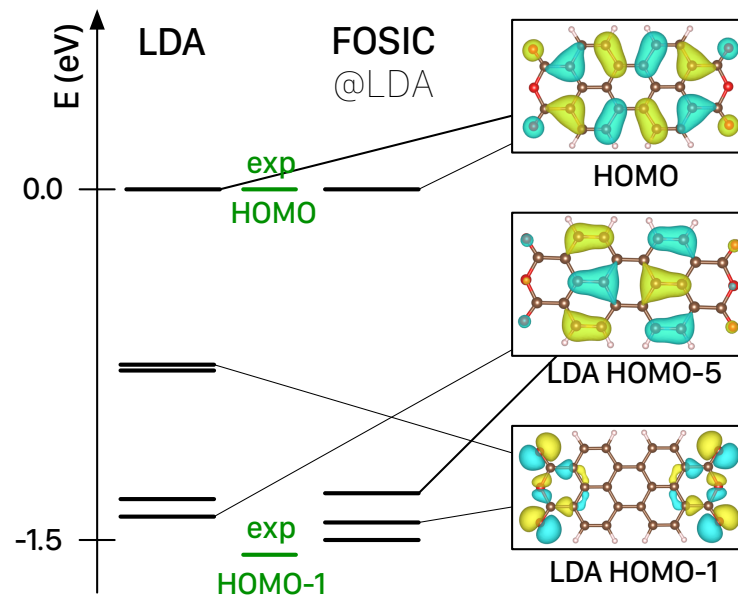
Derivative Discontinuity

Application to molecules

Improved ionization potentials from ϵ_{HOMO}

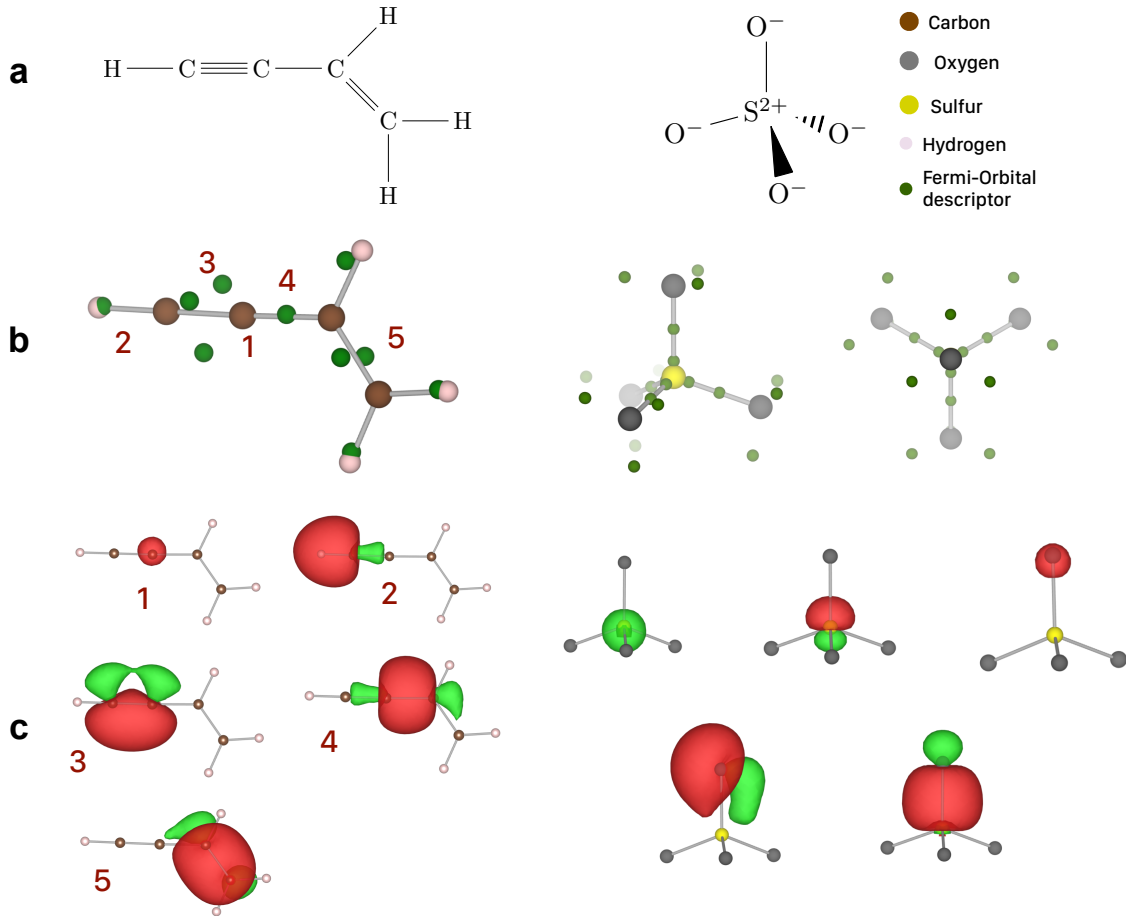


Correct level ordering



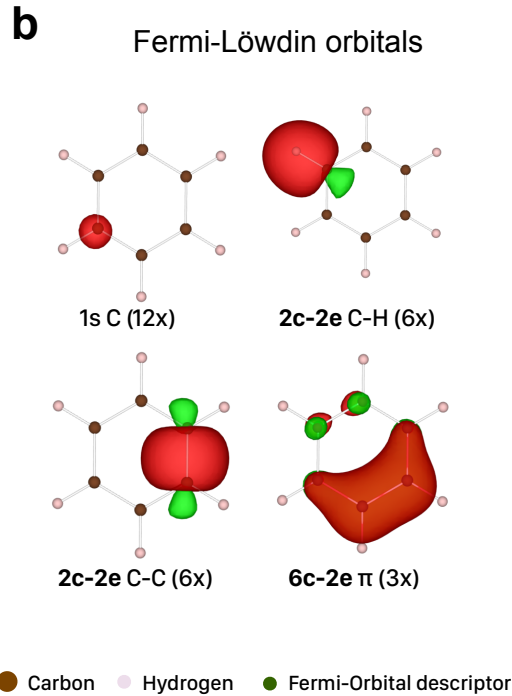
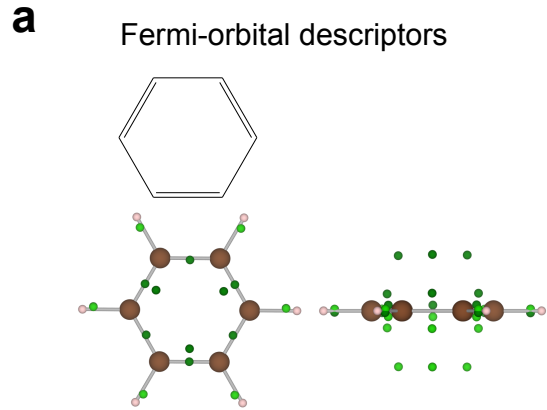
Chemical insights

Fermi-Löwdin orbitals – a simple example

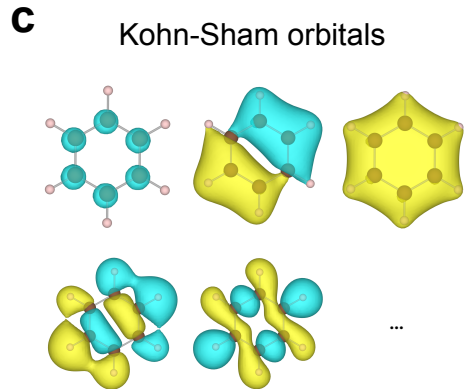


- Fermi orbital descriptors can be seen as electronic positions
- Descriptors of 1s core close to nuclear positions
- Single bond: rotational symmetric, double and triple bond: ‘banana’-like shapes
- SO_4^{2-} : four equivalent, single bonded oxygen (Lewis picture)

Kohn-Sham- and Fermi-Löwdin orbitals of Benzen



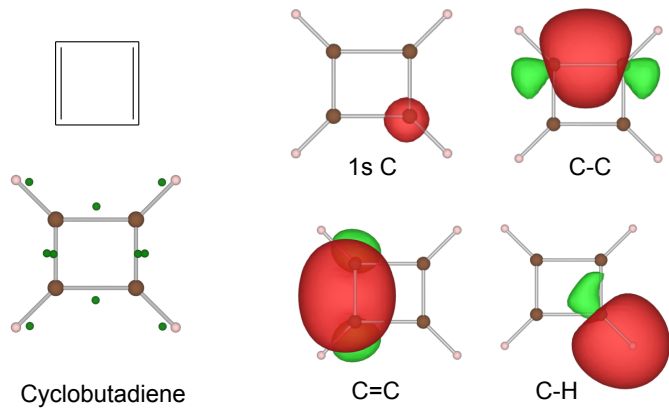
- Fermi orbital descriptors can be seen as electronic positions
- No physical meaning of KS orbitals
- Shape and position of Fermi-orbitals tell bonding details
- 4n+2 rule



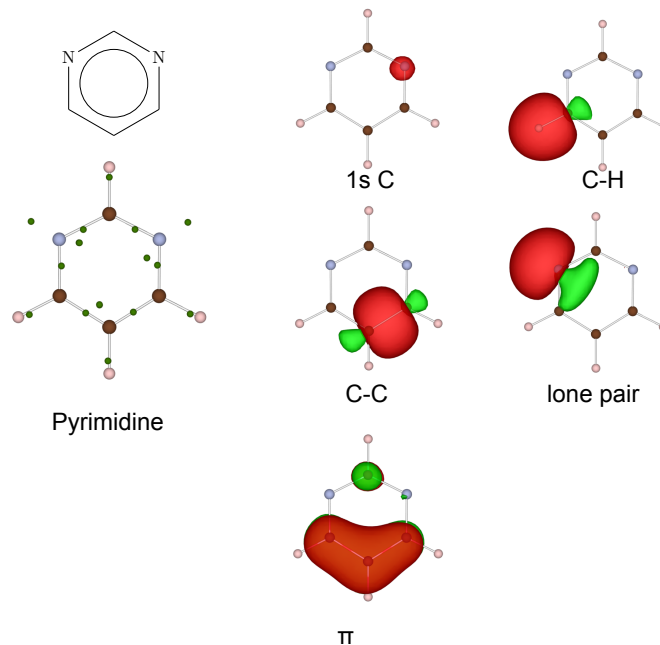
$$E_{\sigma}^X = -\frac{1}{2} \int d^3\mathbf{r} \rho_{\sigma}(\mathbf{r}) \int d^3\mathbf{a} \frac{|F_{i\sigma}(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{a}|}$$

(Anti-) aromatic compounds

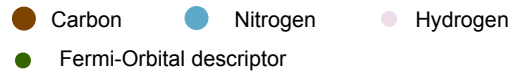
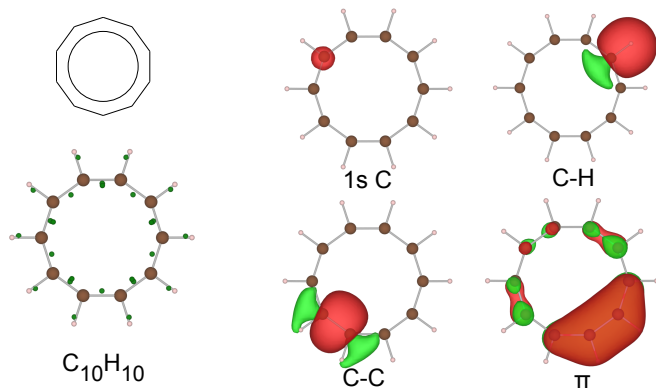
a



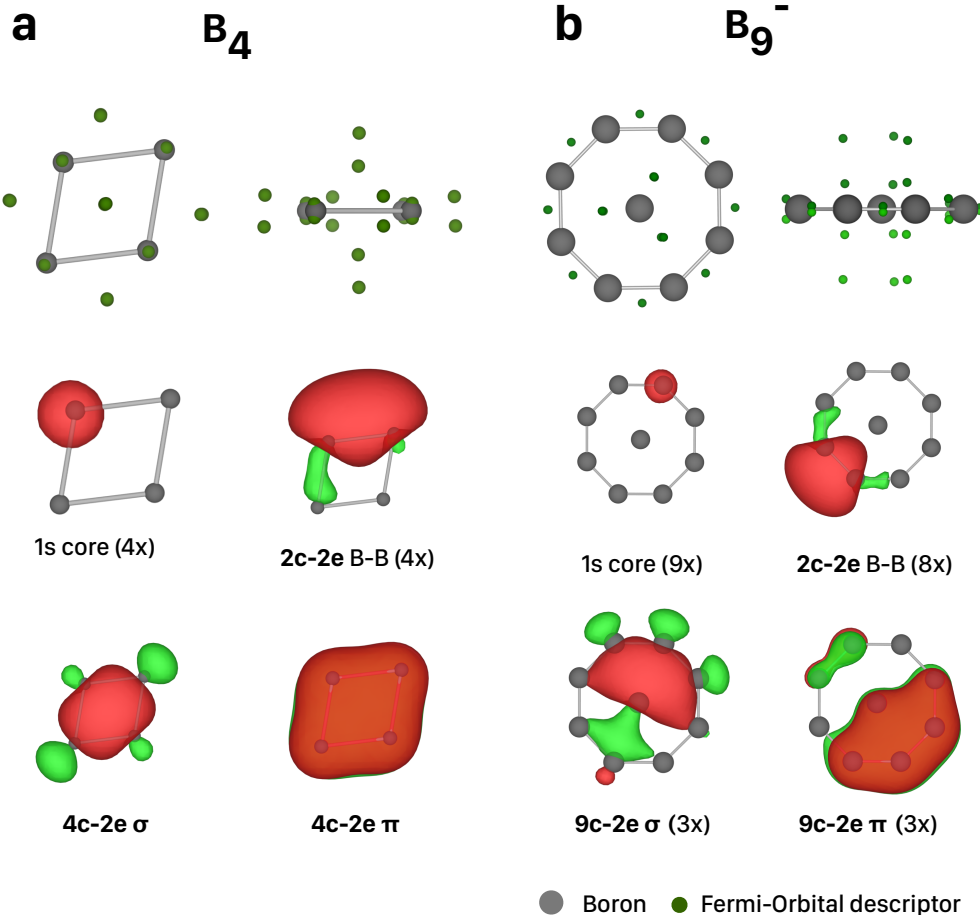
b



c



Bond analysis in Boron clusters

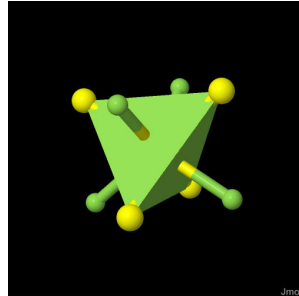
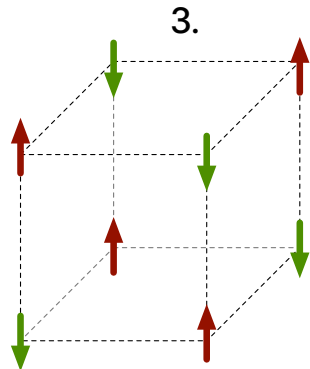
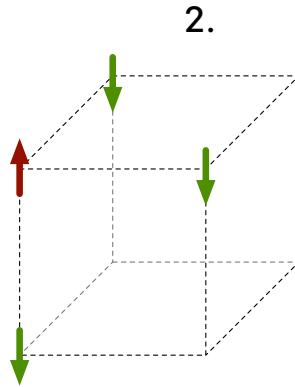
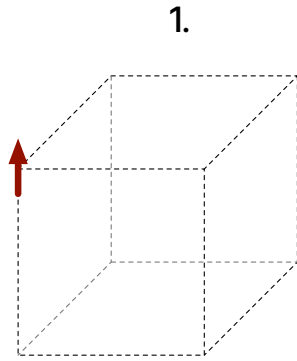


- Yields natural description of bonds in terms of m center- n electron bonds
- Correctly covers multi-center bonds
- No extra parameters or analysis steps needed, its just the result of a FLO-SIC DFT calculation
- Aromatic? \rightarrow Yes ($4n+2$) !

What else ?

Fermi-orbitals – What else can we do with them?

Fermi orbital descriptors of atoms:



- FOD positions with minimum energy are “connected”
- Position of one descriptor defines position of the others
- → correlated, have non-local properties

Can we use this ?

Correlation correction with Fermi-Löwdin orbitals

1. Fermi-Löwdin orbitals yield single electron densities

$$n_k(\mathbf{r}) = |\phi_k(\mathbf{r})|^2 \quad n_T(\mathbf{r}) = \sum_k n_k(\mathbf{r})$$

2. Use LDA* correlation subroutine to calculate E_c for the single electron densities

3. Subtract these energies from E_c of the total density

$$E_c^{\text{corr.}} = E_c^{\text{LDA}} [n_T(\mathbf{r})] - \sum_k E_c^{\text{LDA}} [n_k(\mathbf{r})]$$

* ... or any other functional

Single electron system:

$$|\phi(\mathbf{r})|^2 = |\psi(\mathbf{r})|^2$$

$$n_T(\mathbf{r}) = n_k(\mathbf{r})$$



$$E_c^{\text{corr.}} = 0$$

! exact result !

Correlation correction with Fermi-Löwdin orbitals

Atoms and small molecules (energies in Ha)

	exact*	LDA	Error (%)	FLO-Corr.	Error (%)
He	-0.042	-0.111	164	-0.053	26
B	-0.095	-0.224	135	-0.107	12
N	-0.186	-0.426	130	-0.203	10
Ne	-0.394	-0.739	87	-0.458	16
Na	-0.399	-0.801	100	-0.440	8
Mg	-0.442	-0.887	100	-0.504	10
Ar	-0.731	-1.423	94	-0.828	14
N ₂	-0.549	-0.940	71	-0.613	11
LiF	-0.441	-0.827	87	-0.501	13

- Reduced MAE:
107 % → 13 %
- Computational cheap
- Applicable to any semilocal functional

* D. P. O'Neil, P.M.W. Gill, Mol. Phys., 103, 763 (2005)

Summary

Fermi-orbital based SIC

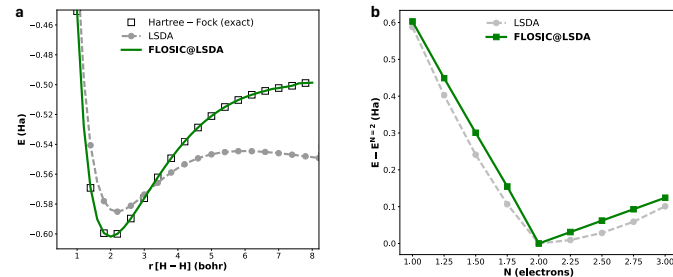
- Correct $\sim 1/r$ behavior of potential
- has correct derivative discontinuity
- Unlike Hubbard-U or range separated hybrids: \mathbf{a}_i are fully determined by variational principle

Chemical insight

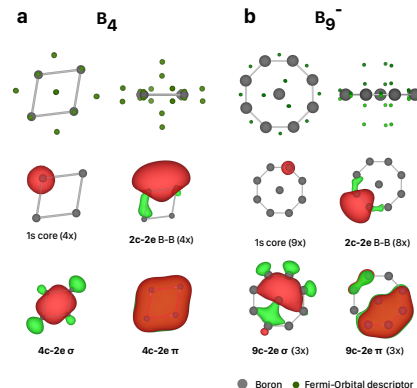
- Yields information about bonding in terms of multi-center multi-electron bonds
- Single-, double-, triple-bond ? Just count descriptors!
- Integral part of the FLO-SIC DFT calculation

Improved correlation energies

- Single electron densities can be used to correct correlation energies
- Computational inexpensive



$$F_{i\sigma}(\mathbf{r}) = \frac{\sum_{\alpha} \psi_{\alpha\sigma}^* \mathbf{a}_{i\sigma} \psi_{\alpha\sigma}(\mathbf{r})}{\sqrt{\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{r})|^2}}$$

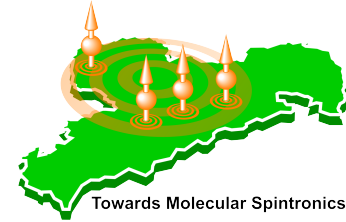


Acknowledgments



The Team

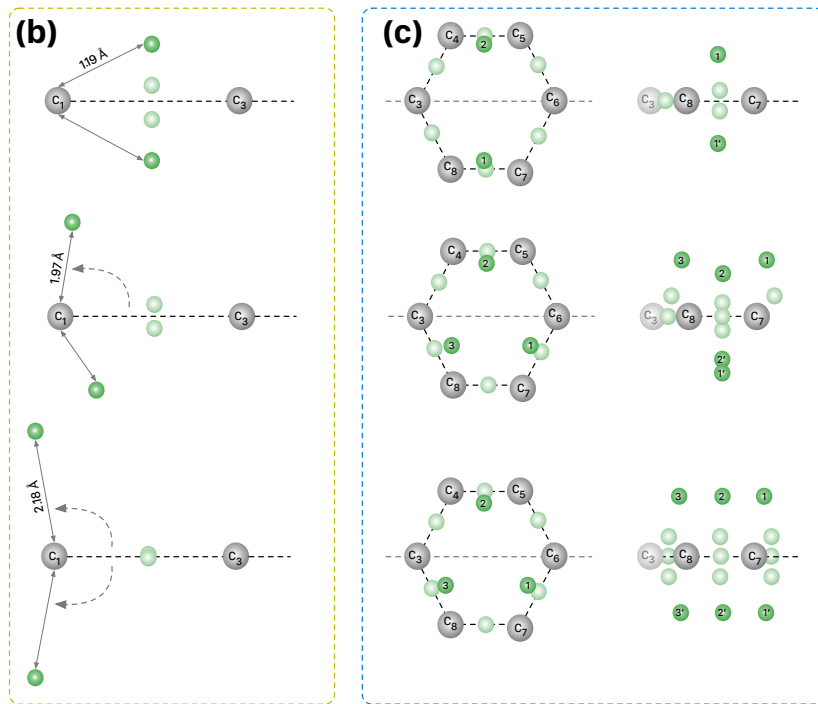
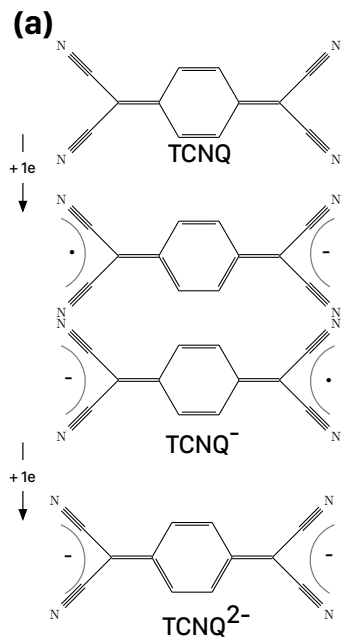
- Mark Pederson (Johns Hopkins)
- Jens Kortus (TU Freiberg)
- Sebastian Schwalbe (TU Freiberg)
- Simon Liebing (TU Freiberg)
- Lenz Fiedler (TU Freiberg)
- Charlotte Vogelbusch (TU Freiberg)
- Der-You Kao (CMU)
- ...



DFG HA 5070/3

Charging of TCNQ Fermi-orbital picture

$$F_{i\sigma}(\mathbf{r}) = \frac{\sum_{\alpha} \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r})}{\sqrt{\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2}}$$



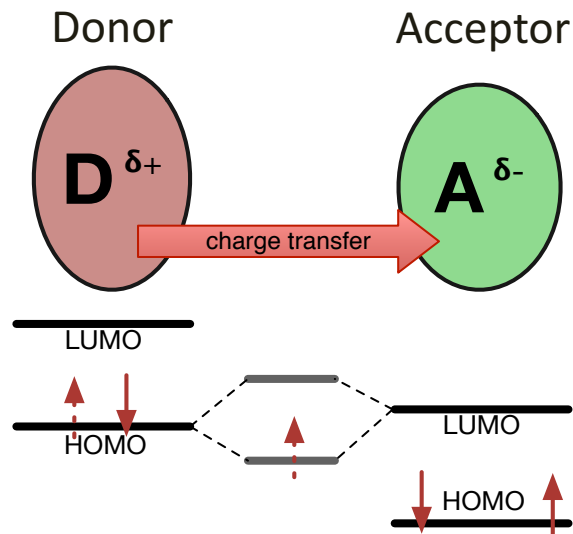
	LDA	FLO-SIC	Exp *
N	-7.3	-10.6	-9.7
N-1	-1.8	-5.3	-3.8
N-2	+2.1	-1.0	--

ϵ_{HOMO} vs. $-IP$ of TCNQ

* W. Kaim and M. Moscherosch, *Coord. Chem. Rev.* **129**, 157 (1994),
Guo-Zu Z., L. Wang., *J. Chem. Phys.* **143**, 221102 (2015).

First principles description of charge transfer compounds ?

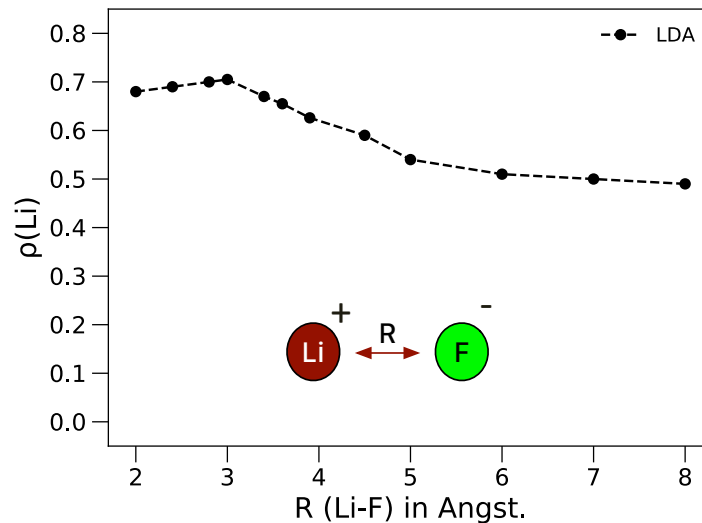
Ground state charge transfer compound



$$E_{\text{HOMO}}(\text{D}) \cong E_{\text{LUMO}}(\text{A})$$

$$E_{\text{Fermi}}(\text{D}) \gg E_{\text{Fermi}}(\text{A})$$

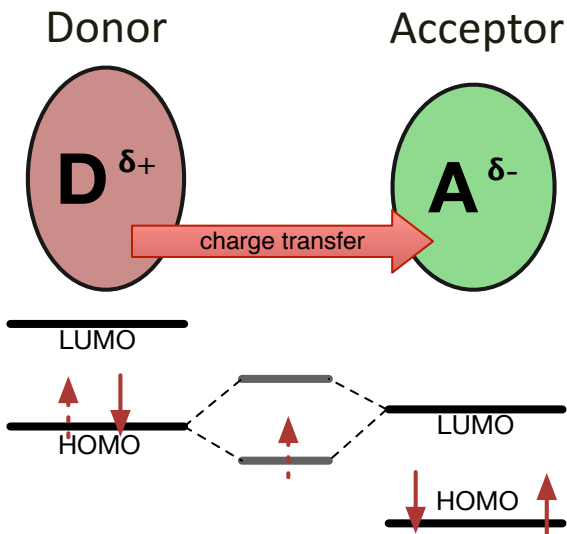
The problem(s) in standard DFT



- No bond breaking
- Li has positive charge at large R
- HOMO (IP) / LUMO (EA) unreliable

First principles description of charge transfer compounds ?

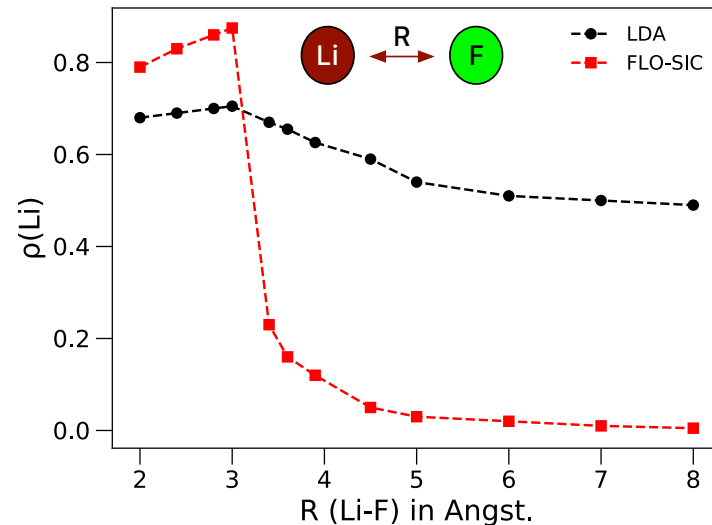
Ground state charge transfer compounds



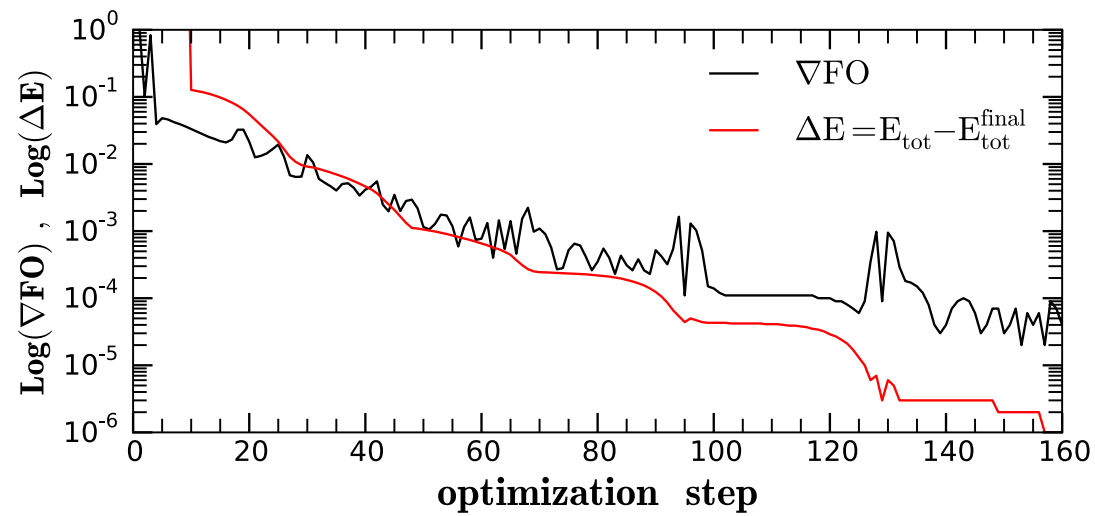
$$E_{\text{HOMO}}(\text{D}) \cong E_{\text{LUMO}}(\text{A})$$

$$E_{\text{Fermi}}(\text{D}) \gg E_{\text{Fermi}}(\text{A})$$

The problem in standard DFT



- Qualitative correct behavior for FLO-SIC
- Bond breaking
- Neutral atom in infinite separations



Fermi-orbital based self-interaction corrected DFT

$$E_{\sigma}^X = -\frac{1}{2} \int d^3\mathbf{r} \rho_{\sigma}(\mathbf{r}) \int d^3\mathbf{a} \left\{ \frac{\rho_{\sigma}(\mathbf{r}, \mathbf{a}) \rho_{\sigma}(\mathbf{a}, \mathbf{r})}{\sqrt{\rho_{\sigma}(\mathbf{r})} \sqrt{\rho_{\sigma}(\mathbf{a})}} \right\} \frac{1}{|\mathbf{r} - \mathbf{a}|}$$

- Perdew 1995: exchange-hole has properties of a single-orbital density

$$F_{i\sigma}(\mathbf{r}) = \frac{\sum_{\alpha} \psi_{\alpha\sigma}^*(\mathbf{a}_{i\sigma}) \psi_{\alpha\sigma}(\mathbf{r})}{\sqrt{\sum_{\alpha} |\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})|^2}}$$

- The Fermi-orbital yields that single-orbital density!
- Fermi-orbitals (Luken and Beratan 1982, Luken and Culberson, 1984) are a special set of localized orbitals
- At $r = a_{i\sigma}$, the square of the FO equals to the total spin density at that point