Self-interaction-correction and the Optimized Effective Potential

Thomas Körzdörfer and Stephan Kümmel
University of Bayreuth, Germany

Definition:
\[ \delta \sigma = E_\text{SI}(\{n_{i}\}) + E_\text{SI}^{\text{corr}}(\{n_{i}\},0) \]

- We call \( \delta \sigma \) the self-interaction energy of the orbital \( \phi_{i} \).
- Note, that for the exact functional \( \delta \sigma \) vanishes for every \( v \)-representable one-particle density.
- Problems:
  - \( \delta \sigma \) does not vanish in general for one-particle densities!
  - \( \delta \sigma \) is of electron self-interaction
  - \( \delta \sigma \) takes different values for different one-particle densities!
  - Unitary invariance problem

Self-interaction correction according to Perdew and Zunger [1]:
\[ E_\text{SI}^{\text{corr}}[\{n_{i}\},\{\psi_{i}\}] = \sum_{i} \sum_{i'} [E_{\text{SI}}[\{n_{i}\},\{\psi_{i}\}]]_{ii'} \]
\[ E_\text{SI}^{\text{corr}}[\{n_{i}\},\{\psi_{i}\}] = \sum_{i} \sum_{i'} [E_{\text{SI}}[\{n_{i}\},\{\psi_{i}\}]]_{ii'} \]
\[ E_\text{SI}^{\text{corr}}[\{n_{i}\},\{\psi_{i}\}] = \sum_{i} \sum_{i'} [E_{\text{SI}}[\{n_{i}\},\{\psi_{i}\}]]_{ii'} \]

- Unitary invariance problem:
- With which orbitals should we construct the total energy?
- At least two reasonable choices:
  - Kohn-Sham orbitals
  - Energy-minimizing orbitals

Standard OEP

Total energy is a functional of the Kohn-Sham orbitals:
\[ E_\text{OEP}^{\text{KSF}} = E_\text{OEP}^{\text{KSF}}[\{\psi_{i}\}] \quad \text{where} \quad \psi_{i} = \text{Kohn-Sham orbitals} \]
\[ E_\text{OEP}^{\text{KSF}} = \sum_{i} \sum_{i'} \int \left[ \frac{\psi_{i}^*(\mathbf{r})}{\psi_{i}(\mathbf{r})} \frac{\partial H_{\text{KSF}}(\mathbf{r})}{\partial \psi_{i}^*(\mathbf{r})} \right] d\mathbf{r} \quad \text{where} \quad G_{\text{KSF}}(\mathbf{r},\mathbf{r}') = \frac{1}{v_{\text{KSF}}(\mathbf{r})} \left[ \psi_{i}^*(\mathbf{r}) \psi_{i}^*(\mathbf{r}') + \frac{\psi_{i}^*(\mathbf{r})}{v_{\text{KSF}}(\mathbf{r})} \right] \]
\[ \text{KLT-approximation} \quad \frac{E_{\text{KSF}}^{\text{KLT}}(n)}{E_{\text{OEP}}^{\text{KSF}}(n)} = \frac{1}{2} \sum_{i} \sum_{i'} \left[ \psi_{i}^*(\mathbf{r}) \psi_{i'}(\mathbf{r}) + \frac{\psi_{i}^*(\mathbf{r})}{v_{\text{KSF}}(\mathbf{r})} \right] \]

Generalized OEP

Total energy is a functional of the energy-minimizing orbitals:
\[ E_\text{OEP}^{\text{GEO}} = E_\text{OEP}^{\text{GEO}}[\{\psi_{i}\}] \quad \text{where} \quad \psi_{i} = \sum_{j} \psi_{j} \quad \text{and} \quad U_{ij} = \text{unitary matrix} \]
\[ E_\text{OEP}^{\text{GEO}} = \sum_{i} \sum_{i'} \int \left[ \frac{\psi_{i}^*(\mathbf{r})}{\psi_{i}(\mathbf{r})} \frac{\partial H_{\text{OEP}}(\mathbf{r})}{\partial \psi_{i}^*(\mathbf{r})} \right] d\mathbf{r} \quad \text{where} \quad G_{\text{OEP}}(\mathbf{r},\mathbf{r}') = \frac{1}{v_{\text{OEP}}(\mathbf{r})} \left[ \psi_{i}^*(\mathbf{r}) \psi_{i}^*(\mathbf{r}') + \frac{\psi_{i}^*(\mathbf{r})}{v_{\text{OEP}}(\mathbf{r})} \right] \]
\[ \text{KLT-approximation} \quad \frac{E_{\text{GEO}}^{\text{KLT}}(n)}{E_{\text{OEP}}^{\text{GEO}}(n)} = \frac{1}{2} \sum_{i} \sum_{i'} \left[ \psi_{i}^*(\mathbf{r}) \psi_{i'}(\mathbf{r}) + \frac{\psi_{i}^*(\mathbf{r})}{v_{\text{OEP}}(\mathbf{r})} \right] \]

PTCDA

PTCDA is an important material for molecular electronic devices!
- Compute density of states (DOS) and compare to experimental data [4].
- LDA and GGA calculations miss energy gap between HOMO and HOMO-1.
- Local density functionals fail for localized orbitals due to their large self-interaction error [3].
- G-KLI and EXX-KLI correctly yield the energy gap, KS-KLI fails badly.

Dissociation of He₂⁺

- Two-center three-electron system
- Common density-functional theories such as LDA show spurious energy-barrier in the dissociation curve due to self-interaction.
- Exact exchange (EXX-KLI) shows wrong dissociation limit (lack of correlation).
- Standard KS-KLI shows wrong eq. bond length and wrong dissociation limit!
- G-KLI improves upon KS-KLI and EXX-KLI

Polarizabilities

- H-1 chains are a well-suited model system for charge-transport properties.
- KS-OEP calculations show excellent agreement with reference MP4-calculations.
- KS-KLI again fails badly.
- How come?
- Self-consistent KS-KLI leads to delocalized KS-orbitals, self-consistent KS-OEP leads to localized KS-orbitals (6)
  - SIC-OEP needs energy-minimizing to work properly!

References