Exchange-Correlation Functionals in DFT

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Duke University

Theory
Biological
Nano
Material

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DOE

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Duke
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Outline

- Kohn-Sham Equations
- Adiabatic Connection for XC: from wave function theory to DFT
- Commonly Used Functionals
- Challenges in DFT from **Fractional Perspectives**
- **LOSC** (Localized orbitals scaling correction)
Kohn-Sham (KS)

\[
\left( -\frac{1}{2} \nabla^2 + v_s(r) \right) |\phi_i\rangle = \varepsilon_i |\phi_i\rangle,
\]

\[v_s(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} + v_J(r) + v_{ext}(r)\]

Generalized Kohn-Sham (GKS)

\[
\left( -\frac{1}{2} \nabla^2 + v_s^{NL}(r, r') \right) |\phi_i\rangle = \varepsilon_i^{GKS} |\phi_i\rangle.
\]

\[v_s^{NL}(r, r') = \frac{\delta E_{xc}[\delta \rho_s(r', r)]}{\delta \rho_s(r', r)} + [v_J(r) + v_{ext}(r)] \delta(r' - r)\]
1. With \( N \) orbitals, the kinetic energy is treated rigorously. In comparison with the Thomas-Fermi theory in terms of density, it is a trade of computational difficulty for accuracy.

2. The KS or GKS equations are in the similar form as the Hartree-Fock equations and can be solved with similar efforts.

3. KS or GKS changes a \( N \) interacting electron problem into an \( N \) non-interacting electrons in an effective potential.

4. The \( E_{xc} \) is not known, explicitly. It is about 10% of the energy for atoms.
Adiabatic connection: from Kohn-Sham reference system to the true physical system

\[ F[\rho] = T[\rho] + V_{ee}[\rho] \]
\[ = T_s[\rho] + J[\rho] + E_{xc}[\rho] \]

So far, the \( E_{xc} \) is expressed in a form that is not appealing, not revealing, not inspiring…

\[ E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \]

What is the relation of the Kohn-Sham reference system to the true physical system?

- The same electron density

\[ \rho(\mathbf{r}) = \sum_{i}^{N} |\phi_i(\mathbf{r})|^2 \]

- Anything else?
Adiabatic connection: from Kohn-Sham reference system to the true physical system

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Adiabatic connection: from Kohn-Sham reference system to the true physical system

\[
\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2
\]

<table>
<thead>
<tr>
<th>Kohn-Sham Reference System</th>
<th>Physical System</th>
</tr>
</thead>
<tbody>
<tr>
<td>the same ( \rho(\mathbf{r}) )</td>
<td>( N \int ds_1dx_2...dx_N</td>
</tr>
<tr>
<td>Hamiltonian ( H_s = \sum_j^N h_s(j) = \sum_j^N -\frac{1}{2}\nabla_j^2 + v_s(\mathbf{r}_j) )</td>
<td>( H = \hat{T} + \hat{V}<em>{ee} + \sum_i^N v</em>{ext}(\mathbf{r}_i) )</td>
</tr>
<tr>
<td>Energy ( E_s = \langle \Psi_s</td>
<td>H_s</td>
</tr>
<tr>
<td>( E_s = T_s[\rho] + \int d\mathbf{r} v_s(\mathbf{r}) \rho(\mathbf{r}) )</td>
<td>( E = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) )</td>
</tr>
<tr>
<td>connecting ( H_\lambda )</td>
<td>( \sum_j^N -\frac{1}{2}\nabla_j^2 + \lambda \hat{V}<em>{ee} + \sum_i^N v</em>\lambda(\mathbf{r}<em>i) ), keeping fixed density ( \rho</em>\lambda(\mathbf{r}) = \rho(\mathbf{r}) )</td>
</tr>
<tr>
<td>( H_0 = H_s )</td>
<td>( H_1 = H )</td>
</tr>
</tbody>
</table>
Adiabatic connection: from Kohn-Sham reference system to the true physical system

\[ H_\lambda = \sum_{j} \frac{-1}{2} \nabla_j^2 + \lambda \hat{V}_{ee} + \sum_{i} v_\lambda (r_i) \]

\[ \frac{\partial E_\lambda}{\partial \lambda} = \frac{\partial \langle \Psi_\lambda | H_\lambda | \Psi_\lambda \rangle}{\partial \lambda} = \langle \Psi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \Psi_\lambda \rangle = \langle \Psi_\lambda | \hat{V}_{ee} + \sum_{i} \frac{\partial v_\lambda (r_i)}{\partial \lambda} | \Psi_\lambda \rangle \]

\[ E_1 - E_0 = \int_{0}^{1} \frac{\partial E_\lambda}{\partial \lambda} d\lambda \]

\[ = \int_{0}^{1} \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle d\lambda + \int d r v_{ext}(r) \rho(r) - \int d r v_{s}(r) \rho(r) \]

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<tr>
<td>[ E_s = T_s[\rho] + \int d r v_s(r) \rho(r) ]</td>
<td>[ E = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int d r v_{ext}(r) \rho(r) ]</td>
</tr>
</tbody>
</table>

\[ J[\rho] = \frac{1}{2} \int d r d r' \frac{\rho(r) \rho(r')}{|r-r'|} \]

Finally,

\[ E_{xc}[\rho] = \int_{0}^{1} \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle d\lambda - J[\rho] \]
Adiabatic connection: from Kohn-Sham reference system to the true physical system

\[ E_{xc}[\rho] = \int_{0}^{1} \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle d\lambda - J[\rho] \]

• Exc in terms of wavefunction!

• Compared with

\[ E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \]

• What is the integrand at \( \lambda = 0 \)?

• Starting point to make approximations – DFA (Density functional approximation)
The Local Density Approximation (Kohn-Sham, 1964)

\[ E_{xc}^{LDA}[ho] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})) \]

\( \varepsilon_{xc}(\rho(\mathbf{r})) \) is the XC energy per particle of a homogeneous electron gas of density \( \rho \). It is a function of \( \rho \).

Dirac exchange energy functional

\[ E_x^{LDA}[ho] = -C_D \int \rho(\mathbf{r})^{\frac{4}{3}} d\mathbf{r} \]
Beyond the Local Density Approximation

\[ E^{LDA}_{xc}[\rho] = \int \, dr \rho(r) \varepsilon_{xc}(\rho(r)) \]

<table>
<thead>
<tr>
<th>Method</th>
<th>Expression</th>
<th>Functionals</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>[ E_{xc} = \int , dr , f(\rho) ]</td>
<td>VWN, PW, GGA</td>
</tr>
<tr>
<td>GGA</td>
<td>[ E_{xc} = \int , dr , f(\rho, \nabla \rho) ]</td>
<td>BLYP, PW96, PBE</td>
</tr>
<tr>
<td>Hybrid</td>
<td>[ E_{xc} = c_1 E^\text{HF}<em>x + c_2 E^\text{GGA}</em>{xc} ]</td>
<td>B3LYP, PBE0</td>
</tr>
<tr>
<td>range-separated</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ E_{x}^{B88} = - \sum_{\sigma=\alpha,\beta} \int \rho_{\sigma}^{4/3} \left[ \frac{3}{4} \left( \frac{6}{\pi} \right)^{1/3} + \frac{\beta x_{\sigma}^2}{1 + 6\beta x_{\sigma} \sinh^{-1} x_{\sigma}} \right] \, dr \]

\[ E_{x}^{PBE} = - \int \rho^{4/3} \left[ \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} + \frac{\mu s^2}{1 + \mu s^2 / \kappa} \right] \, dr \]

\[ E_{x}^{HF} = - \frac{1}{2} \sum_{ij\sigma} \int \int \frac{\phi_{i\sigma}^{*}(\mathbf{r}) \phi_{j\sigma}(\mathbf{r}) \phi_{j\sigma}^{*}(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, dr \, dr' \]

\[ E_{xc}^{B3LYP} = 0.2E_{x}^{HF} + 0.8E_{x}^{LDA} + 0.72\Delta E_{x}^{B88} + 0.81E_{c}^{LYP} + 0.19E_{c}^{VWN} \]
Atomization energies for a few selected molecules, mH

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Exp</th>
<th>LSDA</th>
<th>PBE</th>
<th>UHF</th>
<th>MP2</th>
<th>B3LYP</th>
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<tbody>
<tr>
<td>H₂</td>
<td>174.5</td>
<td>180.3</td>
<td>166.7</td>
<td>133.9</td>
<td>165.7</td>
<td>—</td>
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<tr>
<td>Li₂</td>
<td>39.3</td>
<td>37.9</td>
<td>31.7</td>
<td>4.8</td>
<td>25.5</td>
<td>33.5</td>
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<tr>
<td>Be₂</td>
<td>4.8</td>
<td>20.6</td>
<td>15.6</td>
<td>11.2</td>
<td>−1.6</td>
<td>—</td>
</tr>
<tr>
<td>N₂</td>
<td>364.0</td>
<td>427.1</td>
<td>387.6</td>
<td>183.3</td>
<td>368.1</td>
<td>365.6</td>
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<tr>
<td>F₂</td>
<td>62.1</td>
<td>124.6</td>
<td>85.1</td>
<td>−15.9</td>
<td>111.6</td>
<td>57.7</td>
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<tr>
<td>LiH</td>
<td>92.4</td>
<td>96.9</td>
<td>85.2</td>
<td>52.6</td>
<td>86.1</td>
<td>92.9</td>
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<tr>
<td>OH</td>
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<td>197.9</td>
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<td>—</td>
<td>87.8</td>
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<table>
<thead>
<tr>
<th>functional</th>
<th>G3 (kcal/mol)</th>
<th>barriers- (kcal/mol)</th>
<th>T96 ($a_0$)</th>
<th>H bond- (kcal/mol)</th>
<th>$\alpha_{iso}$ (au)</th>
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<tbody>
<tr>
<td>LDA</td>
<td>72.24</td>
<td>14.36</td>
<td>0.0107</td>
<td>3.02</td>
<td>0.78</td>
</tr>
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**GGA and Meta-GGA**

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<th>$\alpha_{iso}$ (au)</th>
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<tbody>
<tr>
<td>BLYP</td>
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<td>7.37</td>
<td>0.0205</td>
<td>1.46</td>
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<tr>
<td>HCTH</td>
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<td>0.48</td>
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<tr>
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</table>
### Mean Absolute Errors (MAE) Thermochemistry (G3 set150), Barriers (HTBH42161 and NHTB38151), Geometries (T96), Hydrogen Bonding and Polarizabilities

<table>
<thead>
<tr>
<th>functional</th>
<th>post-B3LYP</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G3 (kcal/mol)</td>
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<td>(\alpha_{iso}) (au)</td>
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<td>0.0107</td>
<td>3.02</td>
<td>0.78</td>
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<td>TPSSh</td>
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<td>1.36</td>
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</tbody>
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Range-Separated Functionals
Density Functional Theory

- Structure of matter: atom, molecule, nano, condensed matter
- Chemical and biological functions
- Electronic
- Vibrational
- Magnetic
- Optical (TD-DFT)
Density Functional Theory

- DFT is exact and should give agreement with experiment or high-level ab initio calculations in all situations.

- Approximate functionals perform well in many systems but can fail dramatically in other situations.

- This can be traced back to errors of DFA (density functional approximation).

- The understanding of these errors will hopefully lead to new and improved functionals.

- The same challenges for other approximate QM methods.
A large class of problems

- Wrong dissociation limit for molecules and ions
- Over-binding of charge transfer complex
- Too low reaction barriers
- Overestimation of polarizabilities and hyperpolarizabilities
- Overestimation of molecular conductance in molecular electronics
- Incorrect long-range behavior of the exchange-correlation potential
- Charge-transfer excited states
- Band gaps too small
- Diels-Alder reactions, highly branched alkanes, dimerization of aluminum complexes
Error Increases for systems with fractional number of electrons: Yingkai Zhang and WY, JCP 1998

\[ \text{H}_2^+ \] at the dissociation limit

too low energy for delocalized electrons

Savin, in Seminario, “Recent Developments and Applications of Modern DFT”, 1996
DFT for fractional number of electrons from grand ensembles, Perdew, Parr, Levy, and Balduz, PRL. 1982

\[ E_{N+\delta} = (1 - \delta)E_N + \delta E_{N+1} \]
\[ \rho_{N+\delta} = (1 - \delta)\rho_N + \delta \rho_{N+1} \]
Ground State Degeneracy in QM and in DFT

WY, Yingkai Zhang and Paul Ayers, PRL, 2000 — pure states

\[ \Psi_\alpha = \Psi^a, \quad E_\alpha = E(0) + E(1) \]
\[ \Psi_\beta = \Psi^b, \quad E_\beta = E(1) + E(0) \]
\[ \Psi_\gamma = \frac{1}{\sqrt{2}} (\Psi_\alpha + \Psi_\beta) \]
\[ E_\gamma = E(\frac{1}{2}) + E(\frac{1}{2}) = 2E(\frac{1}{2}) \]

Proton A  e
Proton B  e

Proton A  e/2
Proton B  e/2

\[ E(N) : \quad E(\frac{1}{2}) = \frac{1}{2} E(0) + \frac{1}{2} E(1) = \frac{1}{2} E(1) \]
The linearity condition in fractional charges: The energy of $e/2$

$$E(N)$$

$$E\left(\frac{1}{2}\right) = \frac{1}{2} E(1)$$
$E(N)$

Graph showing the energy ($E$) as a function of the number of electrons ($N$). The graph compares the exact solution with a typical LDA/GGA calculation. The energy decreases as the number of electrons increases, with a sharp decrease around $N$.
A dimer, with $\infty$ separation: each monomer has $E(N)$

For $\delta N$-convex, $2E(N + \frac{1}{2}) < E(N) + E(N + 1)$, delocalized

For $\delta N$-concave, $2E(N + \frac{1}{2}) > E(N) + E(N + 1)$, localized
Consequence of Delocalization Error
1. predicts too low energy for delocalized distributions
2. gives too delocalized charge distributions
Define the **Delocalization Error** as the violation of the linearity condition for fractional charges.

*Cohen, Mori-Sanchez and Yang, 2008 Science*
Too low energy for fractional charge systems

- Energy of dissociation of molecular ion: too low
- Charge transfer complex energy: too low
- Transition state energy: too low
- Charge transfer excitation energy: too low
- Band gap: too low
- Molecular conductance: too high
- (Hyper)polarizability for long molecules: too high
- Diels-Alder reaction products, highly branched alkanes, dimerization of aluminum complexes: too high

Cohen, Mori-Sanchez and Yang, 2008 Science
Seeing the delocalization error

Where is the negative charge?
Band Gap

Definition of fundamental gap

\[ E_{\text{gap}}^{\text{integer}} = \{E(N - 1) - E(N)\} - \{E(N) - E(N + 1)\} = I - A \]

\[ E_{\text{gap}}^{\text{deriv}} = \left\{ \frac{\partial E}{\partial N} \bigg|_{N+\delta} - \frac{\partial E}{\partial N} \bigg|_{N-\delta} \right\} \]

\[ E_{\text{gap}}^{\text{integer}} = E_{\text{gap}}^{\text{deriv}}, \text{ Only if } E(N + \delta) \text{ is linear.} \]
**Chemical Potentials**

Cohen, Mori-Sanchez and WY, PRB, 2008

Unified expressions:

\[
\frac{\partial E_v(N)}{\partial N} = \langle \phi_f | H_{\text{eff}} | \phi_f \rangle
\]

\[
E_{g}^{\text{deriv}} = \langle \phi_{\text{lumo}} | H_{\text{eff}} | \phi_{\text{lumo}} \rangle - \langle \phi_{\text{homo}} | H_{\text{eff}} | \phi_{\text{homo}} \rangle
\]

<table>
<thead>
<tr>
<th>Functional</th>
<th>Calculation</th>
<th>[\frac{\partial E_v(N)}{\partial N}]</th>
<th>[E_{g}^{\text{deriv}}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>explicit density functional</td>
<td>[E_{xc} = E_{xc}[^{\rho}(r)]]</td>
<td>KS</td>
<td>[\varepsilon_{f}^{\text{KS}}]</td>
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<tr>
<td>orbital functional</td>
<td>[E_{xc} = E_{xc}[^{\rho_s}(r', r)]]</td>
<td>OEP</td>
<td>[\varepsilon_{f}^{\text{OEP}} + \Delta_{xc}^{f}]</td>
</tr>
<tr>
<td>orbital functional</td>
<td>[E_{xc} = E_{xc}[^{\rho_s}(r', r)]]</td>
<td>GKS</td>
<td>[\varepsilon_{f}^{\text{GKS}}]</td>
</tr>
</tbody>
</table>

- KS orbital gap is equal to the band gap, for any explicit density functional.
- OEP orbital gap is NOT equal to the band gap.
- GKS orbital gap is the band gap, for any orbital functional.

**Gap as the discontinuity of energy derivatives- chemical potentials**
How can fundamental gap be predicted in DFT

For continuous and differentiable functionals of density/density matrix

- **LUMO** energy is the chemical potential for electron addition
- **HOMO** energy is the chemical potential for electron removal
- **Fundamental gaps** predicted from DFT with KS, or GKS calculations, as the KS gap or the GKS gap
- For **orbital functionals**, the LUMO of the KS (OEP) eigenvalue is **NOT** the chemical potential of electron addition. The KS gap is not the fundamental gap predicted by the functional.

\[
\frac{\partial E_v(N)}{\partial N} = \langle \phi_f | H_{\text{eff}} | \phi_f \rangle
\]

WY, Mori-Sanchez and Cohen, PRB 2008, JCP 2012
Convex curve (LDA, GGA):

derivative underestimates $I$, overestimates $A$, $I-A$ is too small

Concave curve (HF):

derivative overestimates $I$, underestimate $A$, $I-A$ is too large

For Linear $E(N)$

$$\Delta N = 1, \quad \Delta E = \frac{\partial E}{\partial N}$$
How well can fundamental gap be predicted in DFT

- **Fundamental gaps** predicted from DFT with KS, or GKS calculations, as the KS gap or the GKS gap

- Only works well if functionals have minimal delocalization/localization error.
Delocalization Error—Size dependent manifestation

A  $\text{H}_2^+$ binding curve

B  H atom with fractional charge

Delocalization Error
Delocalization Error—Size dependent manifestation

Deviations between the calculated $\varepsilon_{HOMO}$ and $-I_{ve}$ and between $I_{ve}$ and $I_{exp}$ for a series of $He_M$ clusters (non-interacting).

$$I_{ve} = E(N-1)-E(N)$$

$$\varepsilon_{HOMO} = \left(\frac{\partial E(N)}{\partial N}\right)_v$$

---

Mori-Sancehz, Cohen and Yang PRL 2008, National Science Review 2018
• **Orbitalets**: Novel localized orbitals to represent density matrix.
• **Size-consistent**, functional of the GKS density matrix for corrections to common DFA.
• Accurately characterization of the distributions of *global* and *local* fractional electrons.
• **Systematic improvements**: the dissociation of cationic species, the band gaps of molecules and polymers, the energy and density changes upon electron addition and removal, and photoemission spectra.
Orbitalets: Novel Localized Orbitals

\[ \rho_s = \sum_{ij} \phi_i \langle \phi_i | \rho_s | \phi_j \rangle \langle \phi_j | \phi_i \rangle = \sum_{ij} \lambda_{ij} \phi_i \langle \phi_j \rangle \]

\[ \lambda_{ij} = \langle \phi_i | \rho_s | \phi_j \rangle \]

\[ |\phi_{j\sigma}\rangle = \sum_m U_{jm}^\sigma |\psi_{m\sigma}\rangle \]

E-Constrained Optimization

\[ F = \sum_i \left[ \langle \phi_i | r^2 | \phi_i \rangle - \langle \phi_i | r | \phi_i \rangle^2 \right] + \sum_{im} w_{im} |U_{im}|^2 \]

Space and Energy localization

\[ F = (1 - \gamma) \sum_p \Delta r_p^2 + \gamma C \sum_p \Delta h_p^2 \]

JPCL 2020
Novel Localized Orbitals

**Orbitalets**

-- Span **both occupied and virtual** space

-- Localization **both in the physical space** and in the **energy** space.

Traditional
-- localized orbitals -- localization in the physical space

-- canonical orbitals -- localization only in the energy space (energy eigenstates of an one-particle Hamiltonian)
Delocalization Error—Size dependent manifestation
Distribution of LO densities in $H_2^+$

At small $R$, $R=1\,\text{Å}$
- Large energy gap between HOMO and LUMO
- Little mixing, LO ~ Canonical Orb, integer occupations

At large $R$, $R=5\,\text{Å}$
- Small energy gap between HOMO and LUMO
- Much mixing, LO localized, fractional occupations
The GSC/LSC has the following asymptotic form,

\[ \Delta E_{\text{GSC}}^\Delta = \frac{1}{2} \kappa \left( n_f - n_f^2 \right), \]  

(2)

\[ \Delta E_{\text{LSC}}^\Delta \approx \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \tilde{n}_f(\mathbf{r}) \left[ 1 - \tilde{n}_f(\mathbf{r}') \right] \tilde{\kappa}(\mathbf{r}, \mathbf{r}'). \]  

(3)

\[ \frac{\partial^2 \Delta E_{\text{GSC}}^\Delta}{\partial n_f^2} = -\kappa \]

\[ \frac{1}{2} \kappa = \frac{1}{2} \int \int \frac{\rho_f(\mathbf{r})\rho_f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{C_x}{3} \int [\rho_f(\mathbf{r})]^{\frac{4}{3}} d\mathbf{r}, \]
New LOSC, as correction to DFA

\[ \Delta E^{\text{LOSC}} = \sum_{ij} \frac{1}{2} \kappa_{ij} \lambda_{ij} (\delta_{ij} - \lambda_{ij}) = \frac{1}{2} \text{tr}(\kappa \omega) \]

\[ \frac{1}{2} \kappa_{ij} = \frac{1}{2} \int \int \frac{\rho_i(r)\rho_j(r')}{|r-r'|} \, dr \, dr' - \frac{\tau C_x}{3} \int [\rho_i(r)]^{2/3} [\rho_j(r)]^{2/3} \, dr \]

Non-empirical parameter to get correct limit for \( H_2^+ \)

\[ \tau = 6(1 - 2^{-1/3}) \approx 1.2378 \]

Orbital energy corrections

\[ \Delta \epsilon_m = \sum_i \kappa_{ii} \left( \frac{1}{2} - \lambda_{ii} \right) |U_{im}|^2 - \sum_{i \neq j} \kappa_{ij} \lambda_{ij} U_{im} U_{jm}^* \]
Linear $E(N)$ and Size-Consistent: $He_2(R)$

![Graphs showing linear energy vs. number of electrons for $He_2$ at different distances ($R=1\text{Å}, 2\text{Å}, 3\text{Å}, 5\text{Å}$).](image)

- **Energy (a.u.)**
- **Number of electrons**

**Legend:**
- BLYP
- LOSC-BLYP
- CCSD(T)
LOSCL: Linear $E(N)$ and Size-Consistent

(a) $\varepsilon_{\text{HOMO}} + I_{\text{ve}}$ (eV)

$\Delta I = I_{\text{ve}} - I_{\text{exp}}$ (eV)

He, He$_2$, He$_4$, He$_8$, He$_{16}$, He$_{M \rightarrow \text{Inf}}$
(a) G2-97 set

Ref. $-I_{ve}$ and $-A_{ve}$ (eV)

- LOSC-LDA
- LDA
LOSCL: HOMO, LUMO and Energy Gaps
LOSC: HOMO, LUMO and Energy Gaps

(c) polyacene

Exp
LOSC-LDA
LDA
<table>
<thead>
<tr>
<th>Method</th>
<th>IP</th>
<th>EA</th>
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<tbody>
<tr>
<td>scGW</td>
<td>0.47</td>
<td>0.34</td>
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<tr>
<td>$G_0W_0$-PBE</td>
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<td>LOSC-BlLYP</td>
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<td>BLYP</td>
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<tr>
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<td>2.44</td>
</tr>
</tbody>
</table>

Mean absolute error (eV) of ionization potential and electron affinity results on 40 test molecules.
Photoemission spectrum of nitrobenzene

Photoemission spectrum of anthracene
Photoemission spectrum of C60
Photoemission spectrum of H$_2$TPP
LOS: photoemission spectra

(d) Exp

LOS: LDA

LDA
LOSC: corrections to electron density

$\text{Cl}^- \cdot (\text{H}_2\text{O})_6$

- **PBE**: $\Delta q(\text{Cl}) = 0.04$
- **B3LYP**: $\Delta q(\text{Cl}) = -0.67$
- **LOSC-PBE**: $\Delta q(\text{Cl}) = -0.92$
- **CCSD**: $\Delta q(\text{Cl}) = -0.96$
Self-Consistent Calculation of the Localized Orbital Scaling Correction for Correct Electron Densities and Energy-Level Alignments in Density Functional Theory

Yuncai Mei, Zehua Chen, and Weitao Yang

![Graph showing binding energy and Mulliken charge vs. bond distance for Li-F system]
Donor (1,4-benzenediamine)

Accepter (tetracyanoethylene)

(a) Mulliken charge

(b) Relative total energy

(a) IP

(b) EA
LOSC: Summary

--Very different from conventional density functionals

--Novel localized Orbitals with energy and space localization – *Orbitalets*

--Functional of the Generalized Kohn-Sham density matrix

--Size-consistent
Prospective of DFT Approximations—bright future

Strategy of nonlocal corrections

---Imposing the exact constraints of fractional charges and fractional spins

Semilocal functionals + Nonlocal corrections

• LOSC: Eliminating delocalization error
  • Band gaps
  • Energy alignment
  • Charge transfer
  • ....

• Describing strong correlation (static correlation) — using fractional spins (PNAS, 2018)