Analytical Gradients
in a Subsystem Formulation of DFT

Andreas W. Götz

Theoretische Chemie
Vrije Universiteit Amsterdam

Rijksuniversiteit Groningen
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Motivation

2 Analytical Gradients in Kohn–Sham Density Functional Theory

3 Analytical Gradients in Subsystem Density Functional Theory

4 Test calculations

5 Outlook
Motivation

Why energy gradients (wrt nuclear coordinates)?

- The geometry of a molecule determines many of its physical and chemical properties
- The ground state geometry can be found by geometry optimization
- Efficient geometry optimization requires knowledge of the gradients

- (Numerical) differentiation of the gradient yields the Hessian
  - characterization of stationary points on the PES
  - Harmonic vibrational spectra

- Gradients allow molecular dynamics simulations
Motivation

Why analytical gradients?

Numerical gradients
- Trivial and straightforward implementation
- Highly inefficient (computationally very expensive)
- Can suffer from numerical instabilities

Analytical gradients
- Complicated expressions
- Considerable programming effort
- Superior numerical stability
- Very efficient (computationally cheap)
Motivation

Why Subsystem DFT?

- Demand for efficient simulation methods capable of covering several length- and time-scales

Available electronic structure methods

- Very reliable
- Computationally too demanding

Available classical or multilevel methods like QM/MM

- Very efficient
- Rely on parametrizations $\Rightarrow$ not universally applicable
- Polarization and charge transfer usually neglected

Subsystem DFT

- Full system described on a quantum mechanical basis
- Includes electronic coupling between different subsystems

Motivation

Analytical Gradients in Kohn–Sham Density Functional Theory

Analytical Gradients in Subsystem Density Functional Theory

Test calculations

Outlook
Kohn–Sham DFT energy

\[ E[\rho] = T_s[\rho] + \int v_{\text{ext}}(r) \rho(r) \, dr + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr' + E_{\text{xc}}[\rho] + E_{\text{NN}} \]

Expression for the electron density

\[ \rho(r) = \sum_{i}^{\text{occ}} n_i |\psi_i(r)|^2 \]

Minimize the Kohn–Sham DFT energy \( E \) with respect to \( \rho \), keep the MOs orthonormal / density normalized

\[ \frac{\delta E[\rho]}{\delta \rho} = 0, \quad S_{ij} = \int \psi_i^*(r)\psi_j(r) \, dr = \delta_{ij} \]
Variationally optimize the Kohn–Sham Lagrangian

\[ L[\rho] = E[\rho] - \sum_{ij} \varepsilon_{ij} (S_{ij} - \delta_{ij}), \quad \frac{\delta L[\rho]}{\delta \psi_i(\mathbf{r})} = 0 \]

⇒ Kohn-Sham equations

\[ \left[-\frac{1}{2} \nabla^2 + v_s(\mathbf{r})\right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \]

Kohn–Sham single-particle potential

\[ v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}) \]
Analytical gradient of the Kohn–Sham DFT energy

- Derivative with respect to a nuclear coordinate $R_{A_k}$

$$\frac{dE[\rho]}{dR_{A_k}} = \frac{dL[\rho]}{dR_{A_k}} = \frac{\partial L[\rho]}{\partial R_{A_k}} + \sum_i \int \frac{\delta L[\rho]}{\delta \psi_i(r)} \frac{\partial \psi_i(r)}{\partial R_{A_k}} \, dr$$

$$= \frac{\partial L[\rho]}{\partial R_{A_k}} = \frac{\partial E[\rho]}{\partial R_{A_k}} - \sum_i \frac{\varepsilon_i}{\partial S_{ii}}$$

...we obtain for the partial derivative

$$\frac{\partial E[\rho]}{\partial R_{A_k}} = Z_A \sum_{B \neq A} \frac{Z_B (R_{B_k} - R_{A_k})}{|R_B - R_A|^3} + \int \frac{\partial v_{\text{nuc}}(r)}{\partial R_{A_k}} \rho(r) \, dr$$

$$- \sum_{i}^{\text{occ}} n_i \int \frac{\partial \psi_i(r)}{\partial R_{A_k}} \nabla^2 \psi_i(r) \, dr + \int v_s(r) \frac{\partial \rho(r)}{\partial R_{A_k}} \, dr$$
Motivation

Analytical Gradients in Kohn–Sham Density Functional Theory

Analytical Gradients in Subsystem Density Functional Theory

Test calculations

Outlook
Subdivide the total system into appropriately chosen subsystems

\[ \rho_{\text{tot}}(r) = \sum_{I}^{M} \rho_I(r) \]

Total energy in subsystem DFT

\[ E[\rho_1, \ldots, \rho_M] = \sum_{I}^{M} E_I[\rho_I] + E_{\text{int}}[\rho_1, \ldots, \rho_M] \]

\( E_I[\rho_I] \): standard KS-DFT energy expression for isolated subsystem \( I \)
Subsystem Density Functional Theory

- **Interaction energy**

\[
E_{\text{int}}[\rho_1, \ldots, \rho_M] = \sum_{I<J} \sum_{A,B} \frac{Z_I^A Z_J^B}{|\mathbf{R}_A^I - \mathbf{R}_B^J|} + \sum_{I \neq J} \int v_{\text{num}}^I(\mathbf{r}) \rho_J(\mathbf{r}) \, d\mathbf{r}
\]

\[
+ \sum_{I<J} \int \frac{\rho_I(\mathbf{r}) \rho_J(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}'
\]

\[
+ T_{s}^{\text{nadd}}[\rho_1, \ldots, \rho_M] + E_{\text{xc}}^{\text{nadd}}[\rho_1, \ldots, \rho_M]
\]

- **Non-additive kinetic energy** (similar for XC)

\[
T_{s}^{\text{nadd}}[\rho_1, \ldots, \rho_M] = T_{s}[\rho_{\text{tot}}] - \sum_{I} M T_{s}[\rho_I]
\]

- **Orbitals of the total system are not known**

  \[\Rightarrow\] **approximate, explicit density functionals for** \( T_{s}^{\text{nadd}} \)
Expansion of the electron density of subsystem $I$

$$\rho_I(r) = \sum_{i}^{\text{occ}(I)} n_i^I |\psi_i^I(r)|^2$$

Minimize the Subsystem DFT energy with respect to the densities $\rho_I$, keep the subsystem MOs orthonormal / densities normalized

$$\frac{\delta E[\rho_1, \ldots, \rho_M]}{\delta \rho_I} = 0, \quad S_{ij}^I = \int \psi_i^I(r)^* \psi_j^I(r) \, dr = \delta_{ij}$$

Variationally optimize the Lagrangian

$$L[\rho_1, \ldots, \rho_M] = E[\rho_1, \ldots, \rho_M] - \sum_{I}^{M} \sum_{ij}^{\text{occ}(I)} \varepsilon_{ij}^I (S_{ij}^I - \delta_{ij})$$

$$\frac{\delta L[\rho_1, \ldots, \rho_M]}{\delta \psi_i^I} = 0 \quad \forall I$$
Subsystem Density Functional Theory

- Set of $M$ coupled single-particle equations

\[
\left[ -\frac{1}{2} \nabla^2 + v_s^I[\rho_I](r) + v_{\text{emb}}^I[\rho_I, \rho_{\text{tot}}](r) \right] \psi_i^I(r) = \varepsilon_i^I \psi_i^I(r)
\]

- Embedding potential

\[
v_{\text{emb}}^I[\rho_I, \rho_{\text{tot}}](r) = \sum_{J \neq I} v_{\text{nuc}}^J(r) + \sum_{J \neq I} \int \frac{\rho_J(r')}{|r - r'|} dr'
\]

\[
+ \left. \frac{\delta T_s[\rho]}{\delta \rho} \right|_{\rho = \rho_{\text{tot}}} - \left. \frac{\delta T_s[\rho]}{\delta \rho} \right|_{\rho = \rho_I} + \left. \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \right|_{\rho = \rho_{\text{tot}}} - \left. \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \right|_{\rho = \rho_I}
\]

- Equations have to be solved iteratively (cycle through subsystems)
Analytical gradient of the Subsystem DFT energy

- Derivative with respect to a nuclear coordinate $R_{Ak}^I$

$$\frac{dE[\rho_1, \ldots, \rho_M]}{dR_{Ak}^I} = \frac{\partial L[\rho_1, \ldots, \rho_M]}{\partial R_{Ak}^I} = \sum_J \frac{\partial E_J[\rho_J]}{\partial R_{Ak}^I} + \frac{\partial E_{\text{int}}[\rho_1, \ldots, \rho_M]}{\partial R_{Ak}^I} - \sum_J \sum_i \varepsilon_i^J \frac{\partial S_{ii}^J}{\partial R_{Ak}^I}$$

- Standard Kohn–Sham energy gradient of the individual subsystems...

- ...plus gradient of the interaction energy

$$\frac{\partial E_{\text{int}}[\rho_1, \ldots, \rho_M]}{\partial R_{Ak}^I} = Z_A^I \sum_{J \neq I} \sum_B \frac{Z_B^J (R_{Bk}^J - R_{Ak}^I)}{|R_B^J - R_A^I|^3}$$

$$+ \sum_{J \neq I} \int \frac{\partial v_{\text{nuc}}^I(r)}{\partial R_{Ak}^I} \rho_J(r) \, dr + \sum_J \int v_{\text{emb}}^J(r) \frac{\partial \rho_J(r)}{\partial R_{Ak}^I} \, dr$$
\[
\frac{dE}{dR_{A_k}^I} = Z_A^I \sum_{B \neq A} \frac{Z_B^I (R_{B_k}^I - R_{A_k}^I)}{|R_B^I - R_A^I|^3} + \int \frac{\partial \nu_{\text{nuc}}^I (r)}{\partial R_{A_k}^I} \rho_I (r) \, dr \\
- \sum_J \sum_i n_i \int \frac{\partial \psi_i^J (r)}{\partial R_{A_k}^I} \nabla^2 \psi_i^J (r) \, dr \\
+ \sum_J \left[ \psi_s^J (r) + \psi_{\text{emb}}^J (r) \right] \frac{\partial \rho_J^I (r)}{\partial R_{A_k}^I} \, dr - \sum_J \sum_i \varepsilon_i^J \frac{\partial S_{ii}^J}{\partial R_{A_k}^I} \\
+ Z_A^I \sum_{J \neq I} \left( \sum_B \frac{Z_B^J (R_{B_k}^J - R_{A_k}^I)}{|R_B^J - R_A^I|^3} \right) + \int \frac{\partial \nu_{\text{nuc}}^I (r)}{\partial R_{A_k}^I} \left( \sum_{J \neq I} \rho_J (r) \right) \, dr
\]

- Conventional KS-DFT energy gradient
  ⇒ no modification required, restrict to appropriate subsystems

Add missing terms
Possible approximations for selected subsystems $J$

- Nuclear coordinates frozen
  $\Rightarrow$ Compute gradient only with respect to nuclei of subsystems $I \neq J$

- Nuclear coordinates and electron density frozen
  $\Rightarrow$ In addition

$$\frac{\partial \rho_J}{\partial R_{A_k}^I} = \delta_{IJ} \frac{\partial \rho_I}{\partial R_{A_k}^I}$$ and

$$\frac{\partial S_{ii}^J}{\partial R_{A_k}^I} = \delta_{IJ} \frac{\partial S_{ii}^I}{\partial R_{A_k}^I}$$

(also holds if basis functions for the expansion of the Kohn–Sham orbitals of a subsystem $J$ are located only on atoms of this subsystem)
Analytical gradient of the Subsystem DFT energy

Major advantages

- No diagonalization bottleneck in SCF
- Frozen subsystems: efficient description of embedding environment (solvent)
Implementation into ADF

- Modern, object-oriented programming techniques
- Fortran90 with abstract data types to represent fragments (subsystems)
- Efficient numerical integration scheme (grid centered on active subsystem)
- Uses ADF’s efficient parallelization for the numerical integration
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Test calculations

Ammonia–water dimer

**LDA** (SVWN/Thomas–Fermi)
Integration accuracy: 6.0
Gradient convergence: $10^{-4}$ au/Å


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<tr>
<th>Method</th>
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<th>$a$(HON)</th>
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<tbody>
<tr>
<td><strong>W2[1]</strong></td>
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Test calculations

Ammonia–water dimer

**GGA** (PW91/PW91k)
Integration accuracy: 6.0
Gradient convergence: $10^{-4}$ au/Å

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**Kohn–Sham**

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**SSDFT**

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Test calculations

**Formamide dimer**

**LDA (SVWN/Thomas–Fermi)**
Integration accuracy: 6.0
Gradient convergence: $10^{-4}$ au/Å


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Test calculations

Formamide dimer

**GGA** (PW91/PW91k)
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Test calculations

\[ [\text{Li(OH}_2\text{)}_4]^+ \]

- LDA (SVWN/Thomas–Fermi)
  - DZP basis
  - Integration accuracy: 5.0
  - Gradient convergence: $10^{-3}$ au/Å
- No symmetry constraint

**Kohn–Sham**
- approx. tetrahedral
- $d(\text{LiO}) \approx 1.92$ Å

**Subsystem DFT**
- Five subsystems ($\text{Li}^+$ and $\text{H}_2\text{O}$)
- approx. tetrahedral
- $d(\text{LiO}) \approx 1.88$ Å
Motivation

Analytical Gradients in Kohn–Sham Density Functional Theory

Analytical Gradients in Subsystem Density Functional Theory

Test calculations

Outlook
Outlook (or: Where we want to go)

Full subsystem DFT

- Test performance of recently implemented kinetic energy functionals for structure optimizations

Embedding calculations (with frozen subsystems)

- Study environmental effects on structures and vibrational spectra
- Adsorption of molecules on surfaces (frozen cluster model)
- Interactions of drug-like molecules with active sites (frozen protein)
Acknowledgments

People

\begin{itemize}
  \item Christoph R. Jacob
  \item Lucas Visscher
\end{itemize}

Money

\begin{itemize}
  \item NWO via VICI programme
\end{itemize}

Thank you for your attention!