Geometry optimization of polymers via ONIOM based elongation method

Denis Mashkovtsev, Wataru Mizukami, Yuriko Aoki
Kyushu University, Japan

Jacek Korchowiec, Anna Stachowicz-Kuśnierz
Jagiellonian University, Poland

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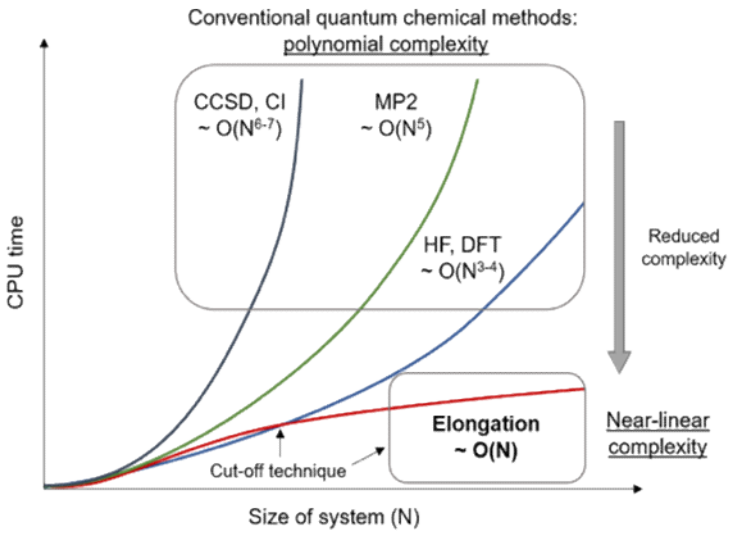
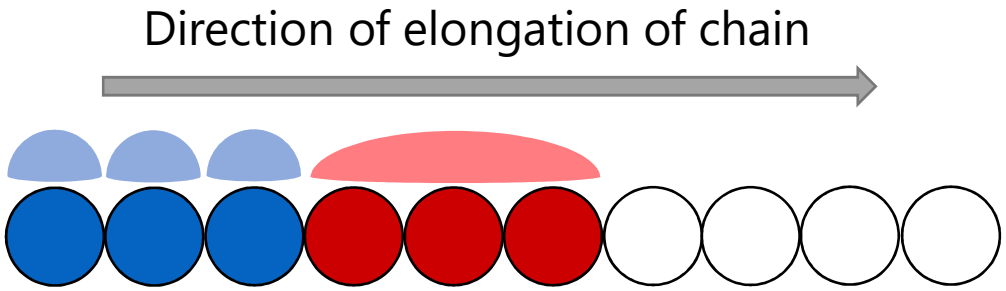
Elongation (ELG): reduced-scaling quantum chemical method for simulation of polymers



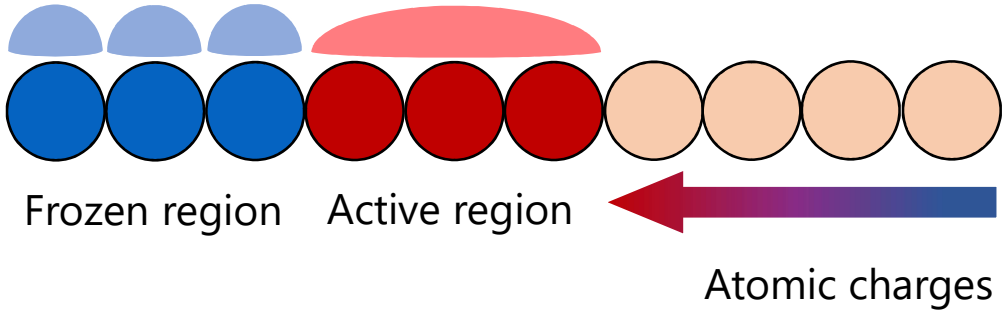


Polymer chain: monomer residues are included to and excluded from the **active** region to keep its constant size

Excluded fragments become **frozen**

Approaches to improvement of ELG

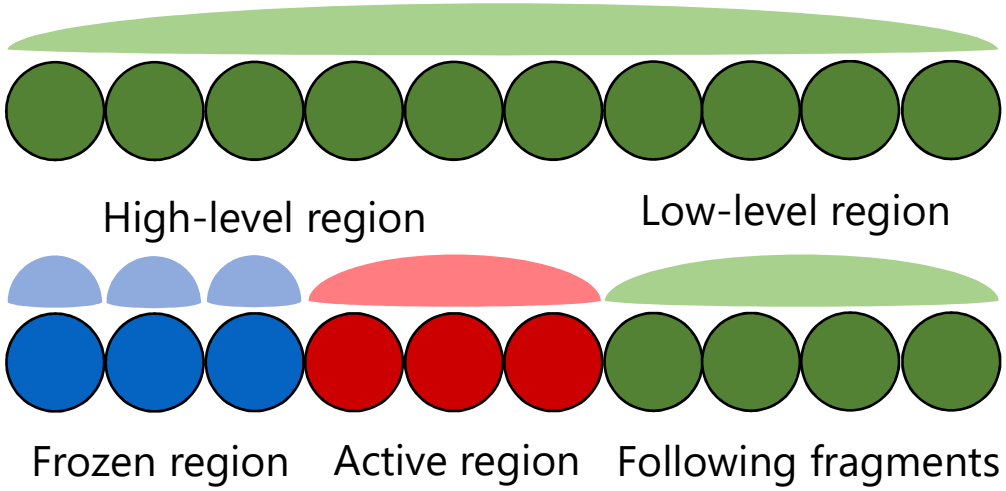
ELG calculation with electrostatic embedding



Atomic charges ← CSA:

CSA – Charge Sensitivity Analysis – approximate parametrical method aimed to reproduce quantum chemical level atomic charges.

ELG calculation with mechanical embedding based on ONIOM method



ONIOM

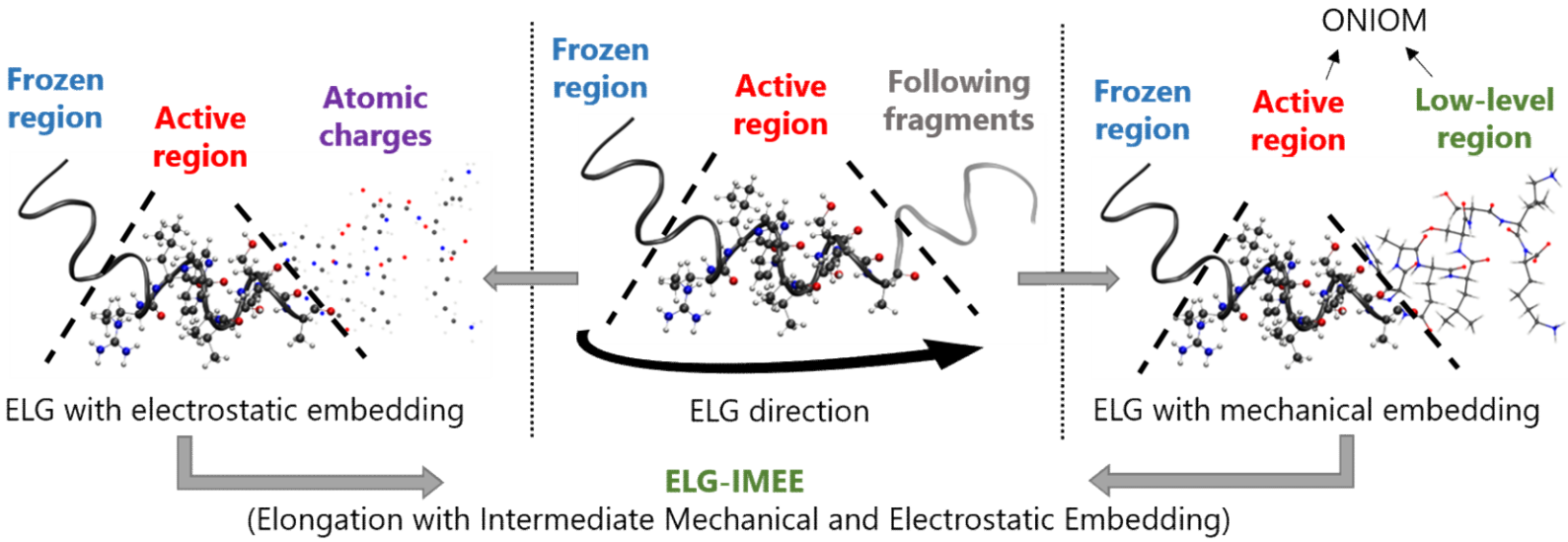
Step 1: whole system is calculated on low level of theory

Step 2: high-level region is recalculated on high level of theory

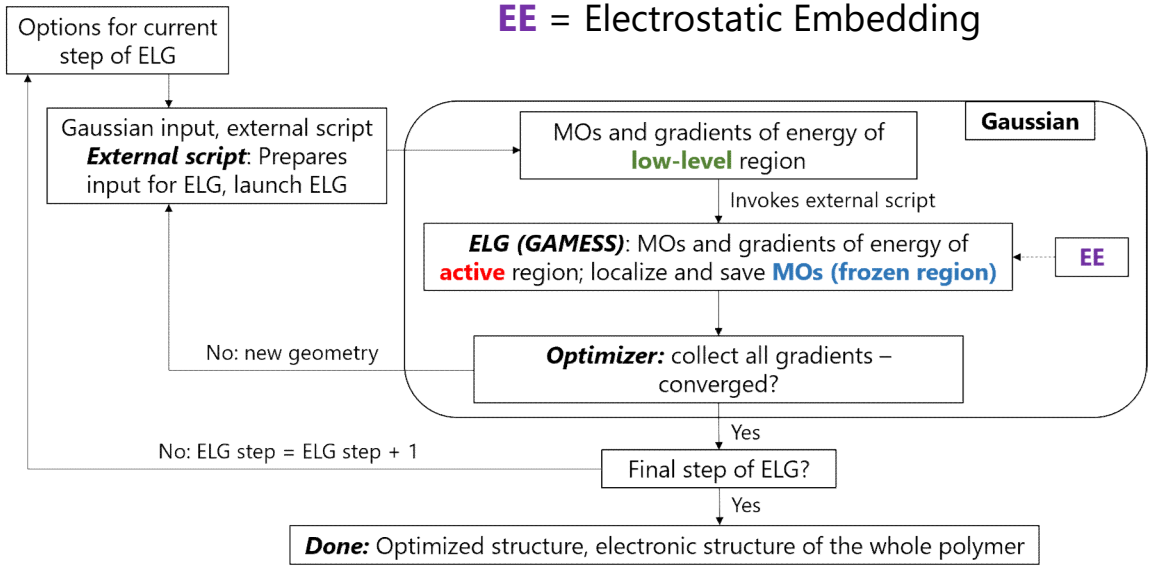
ONIOM equation for electronic energy:

$$E_{ONIOM} = \underbrace{E_{real,low}}_{\text{Step 1}} + \underbrace{E_{model,high}}_{\text{Step 2}} - \underbrace{E_{model,low}}_{\text{Step 2}} \quad (2)$$

ELG-IMEE



EE = Electrostatic Embedding



Computational details:

High-level region
HF/6-31G

Low-level region
PM7

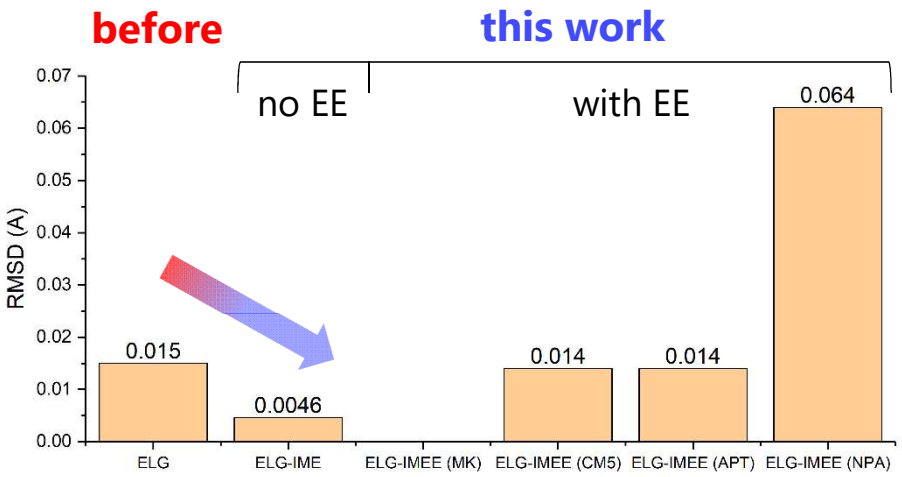
Results of geometry optimization

$$\mathrm{RMSD} = \sqrt{\frac{1}{N_{at}}\left(\sum_{i=1}^{N_{at}}\left(r_i^{ELG} - r_i^{ref}\right)^2\right)}$$

EE = Electrostatic Embedding

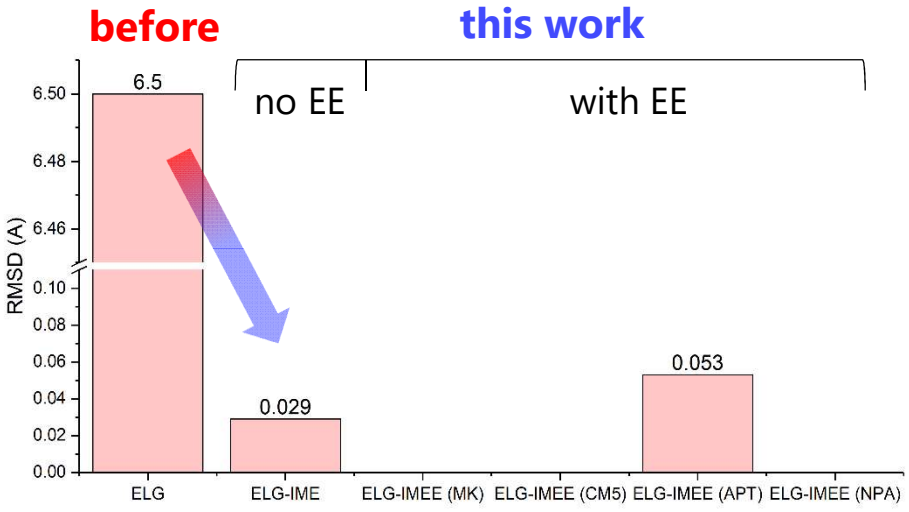
Linear polyethylene chain

- testing system (almost optimized)
- non-polar



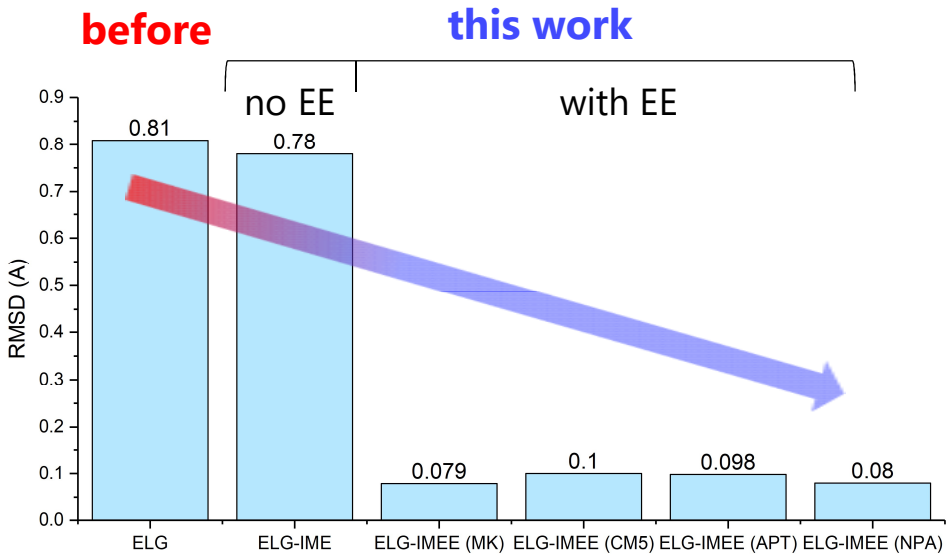
Distorted polyethylene chain

- randomly distorted
- non-polar



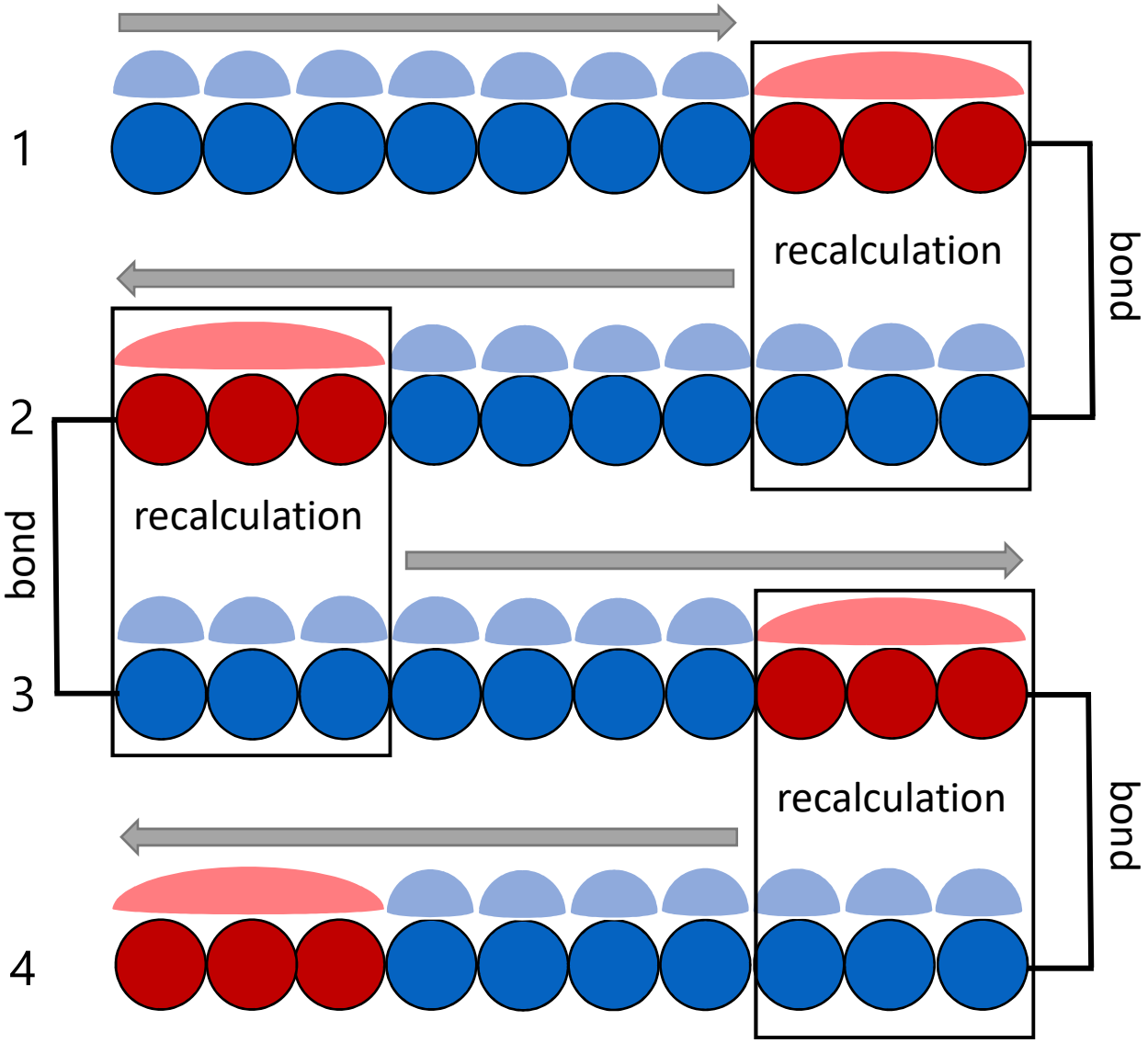
Nylon-6

- randomly distorted
- chain is slightly polarized



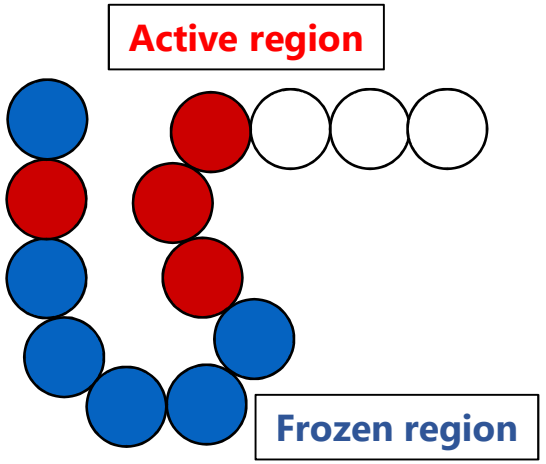
Future plans

Domain decomposition in ELG calculation



Reimplementation of ELG with new algorithm of localization

Current algorithm is inefficient for 3D polymers



ELG in GAMESS → (with new algorithm) PySCF

proof-of-concept

CP2K