Computational Studies on Electronic and Dielectric Properties of Polymer Compounds

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Background

- New polymer materials have potential for the use in the high-voltage technology applications
- Microscopical mechanisms for the electronic and dielectric properties not well understood

- Computational and theoretical approaches are valuable tools in studying these mechanisms

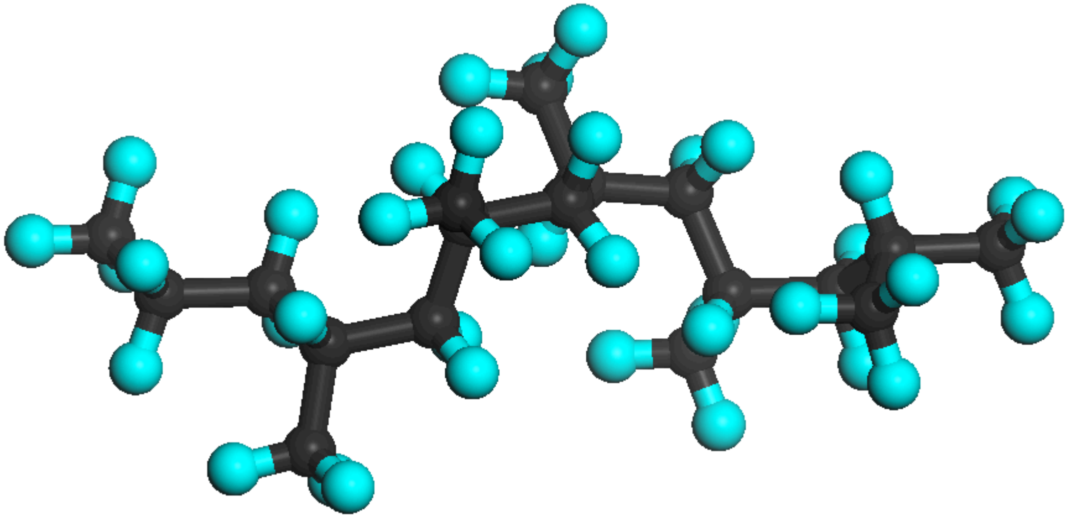
Targets of our computational studies

- Electronic properties of polymers
  - Electronic structure, band gap energy E_g
- Dielectric properties of polymers
  - Dipole moment, polarizability, dielectric constant
- Spectroscopic properties of polymers
  - Absorption spectroscopy (complex dielectric function)

Computational frameworks

- Semi-empirical methods of quantum chemistry:
    - MNDO, MINDO/3, AM1 ja PM3 parameterization (MOPAC package)
    - Molecules containing hundreds of atoms
    - Seems not to predict well electric polarization properties
- Methods based on the density functional theory:
    - Molecular based, first-principles all-electron DFT methods within the generalized gradient approximation (GGA) (Gaussian 03 package)
    - Solid state based, first-principles pseudopotential DFT methods within the GGA (CASTEP package)

Semiempirical vs. DFT results for isotactic polypropylene (IPP)



Optimized structure of a model molecule for IPP: $C_{18}H_{38}$

- Structural properties well predicted with both semi-empirical and DFT methods

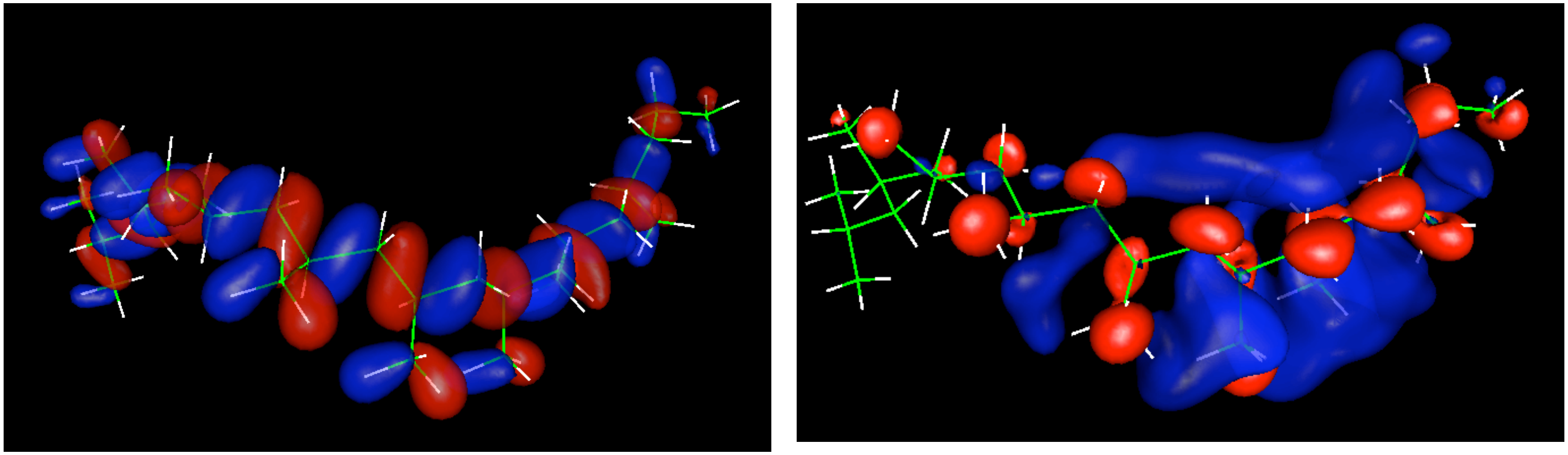
Semiempirical vs. DFT results for electronic properties: Polarizability (α), band gap (E_g) and dielectric constant (ε_r)

Method	α (a_0^3)	E_g (eV)	$\varepsilon_r^{(1)}$
Semi-emp	127	14	1.040
DFT	240	6	1.076

(1) $\varepsilon_r = 1+\{0.892441 \times 10^{-4} \times [\rho \text{ in kg/m}^3]\ [\alpha \text{ in } a_0^3] / [M \text{ in amu}]\}$

- Semi-empirical and DFT results differ significantly
- ε_r too small because the lack of polymer chain-chain interaction (molecular model) and rotation polarization mechanism in calculations

HOMO and LUMO orbitals of a PP model molecule (DFT)

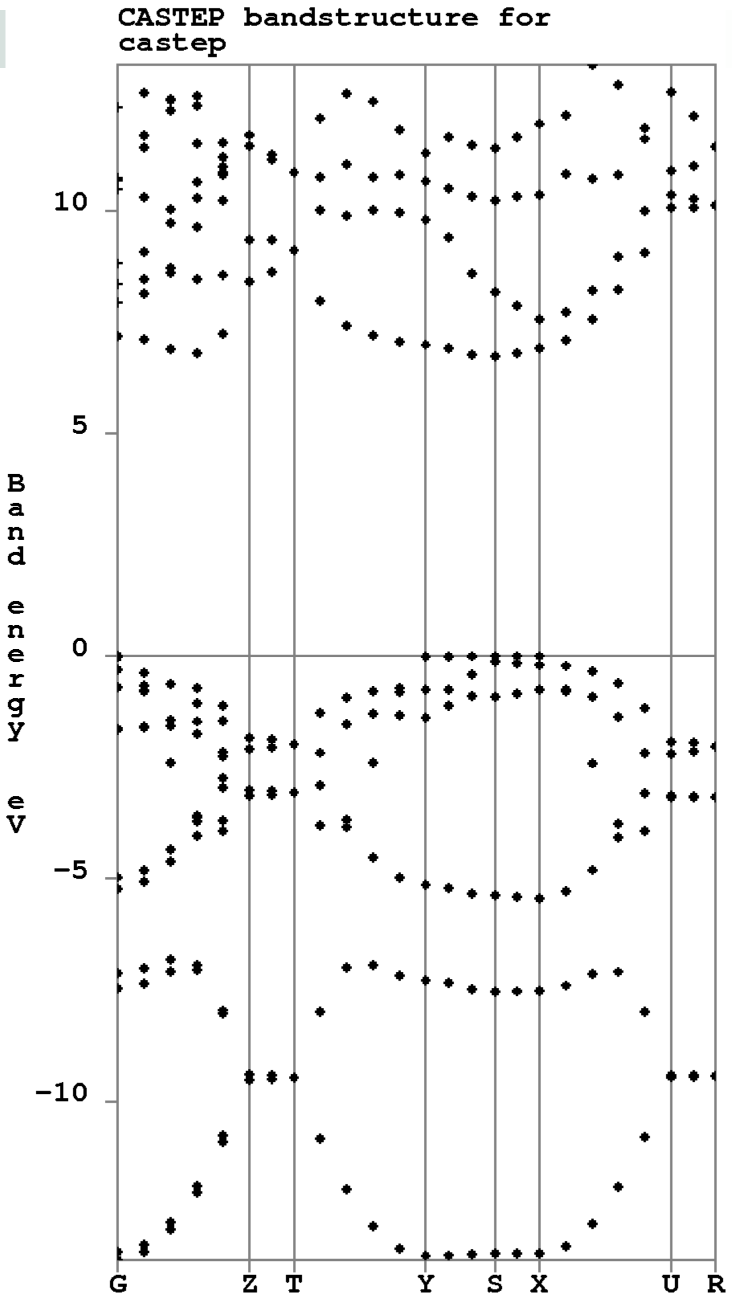


- HOMO orbital is highly delocalized, LUMO orbital more localized
- Geometrical aspects of HOMO and LUMO orbitals can give useful information about the nature of the polarization

DFT PWPP results for orthorhombic polyethylene (PE) crystal: Band structure

Band gap:

*E*g = 6.7 eV (calculated)
*E*g = 7.5 eV (experimental)



Band structure for PE

DFT PWPP results for orthorhombic polyethylene (PE) crystal: Dielectric constant

Dielectric constant ε_r for PE

$\varepsilon_r^{theor}(0)^{(1)}$	$\varepsilon_r^{theor}(0)^{(2)}$	$\varepsilon_r^{experim}(0)$
2.80	2.68	2.4 (40 μm film)

(1) Calculated without scissor operator correction ($\Delta = 0$)
(2) Δ = 7.5 eV (exp.) – 6.7 eV (calculated) = 0.8 eV

=> Theoretical ε_r differs 12% of the experimental value!

Conclusions and future work

- Semi-empirical methods
  - not suitable for studying dielectric properties of polymers
- DFT methods
  - suitable for studying dielectric properties of polymers
  - both molecular and solid state studies
- Future work:
  - DFT calculations for PE and PP with N-containing side groups (CN, NO, NO_2)
  - Calculated absorption spectras
  - Mathematical model for rotation polarization (may be very important for soft matter polarization calculations)