

Intermolecular Forces in Density Functional Theory

Problems of DFT

Peter Pulay at WATOC2005: There are 3 problems with DFT

1. Accuracy does not converge
2. Spin states of open shell systems often incorrect
3. Intermolecular forces often incorrect

Reason: v_{xc}

Intermolecular forces

Crucial for condensed matter, binding, catalysis, surfaces, conformation of macromolecules, solvation etc. etc.

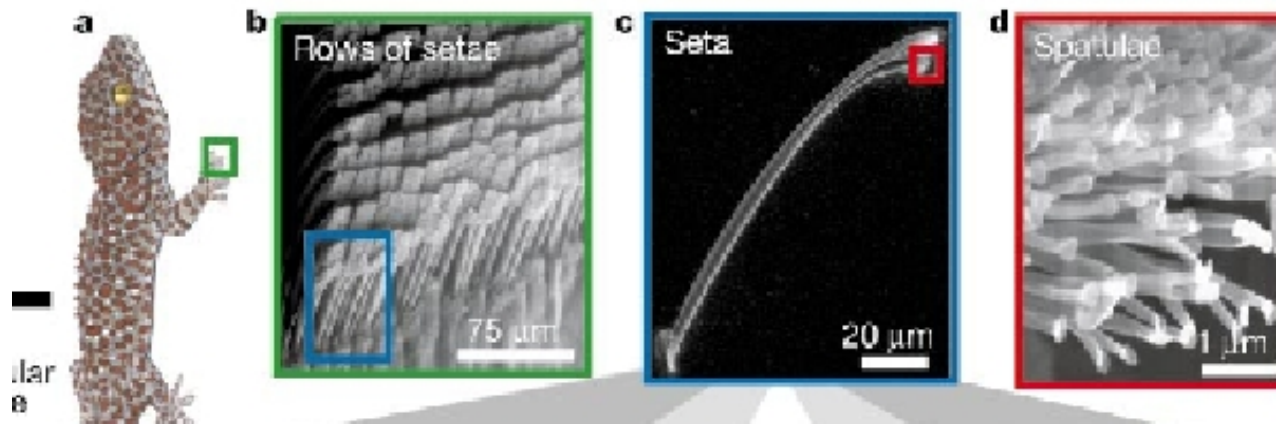
1. Multipole-Multipole (*electrostatics*)
2. Multipole-induced Multipole (*polarizability*)
3. induced Multipole-induced Multipole (*correlation*)
"London Dispersion" forces.

Conventional functionals successful for 1. and 2.

London Dispersion forces

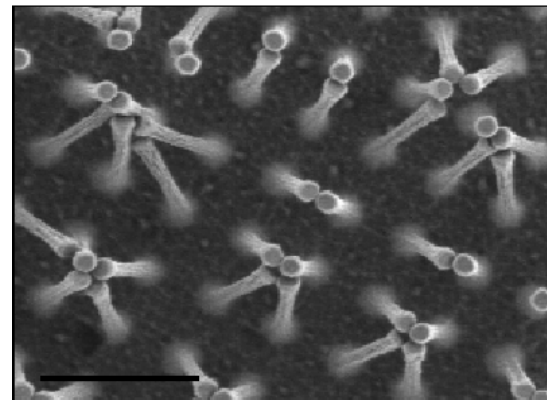
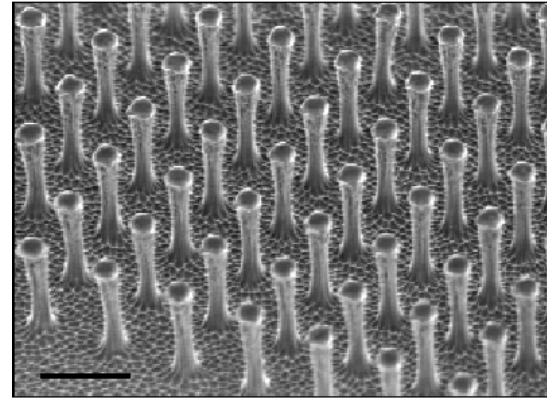
Attractive correlation of instantaneous electron density fluctuations

- act between all molecules
- ubiquitous in condensed phase
- adhesion, surface tension, adsorption, wetting, gases, liquids, thin films
Israelachvili, *Intermolecular and Surface Forces*



Autumn et al. *Nature* **405**, 681 (2000).

Motivation



Polyimide hairs, scale bar = $2 \mu m$.
Geim et al. *Nature materials* 2, 461 (2003).

Can we use DFT?

- "In principle, DFT yields exact ground-state energy including van der Waals energies ..."
Kohn et al. *Phys. Rev. Lett.* **80**, 4153 (1998).
... if the exact exchange-correlation potential was known.
- Kristyan and Pulay (1994), Pérez-Jordá and Becke (1995), and Meijer and Sprik (1996): failure of LDA, GGAs, and hybrid functionals.
- Approaches to solve the problem: "nonlocal vdW"-functional [*Phys. Rev. Lett.* **76**, 102 (1996)], electron density partitioning [*J. Chem. Phys.* **118** 2072 (2003)], SAPT (Symmetry adapted perturbation theory) [*Phys. Rev. Lett* **91**, 33201 (2003)].

but fragmentation necessary or computational cost increased!

Can we use DFT?

Alternative: empirical C_6R^{-6} correction.

- Fragment or atom dependent C_6 coefficients necessary.
- $\{C_6\}$ are related to polarizability of the fragments (condensation temperature increases with Z for rare gases)
→ can be calculated or taken from experiment
- damping function with further parameters is needed
- only energy and forces are corrected, electronic structure remains uncorrected
- problematic for rare events ..
- pairwise potentials do not reproduce many body interaction, *i.e.* $V(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \neq V(\mathbf{r}, \mathbf{r}') + V(\mathbf{r}, \mathbf{r}'') + V(\mathbf{r}', \mathbf{r}'')$
- implemented in CPMD,

`&VDW ... &END`

New approach

Optimization of atom centered potentials:

- *J Chem Phys* **122**, 14113 (2005); *Phys Rev Lett* **93**, 153004 (2004); *Phys Rev B* **71**, 195119 (2005).
- extend your conventional exchange-correlation potential by an atom centered nonlocal potential

$$\hat{v}_{xc}^{\text{DC}} = \hat{v}_{xc}^{\text{conv}} + \sum_{\mathbf{I}} V_{\mathbf{I}}^{\text{ACP}},$$

- for convenience of the form of a pseudopotential

$$V_{\mathbf{I}}^{\text{ACP}}(\mathbf{r}, \mathbf{r}') = V^{(\text{loc})}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + \sum_l V_l^{(\text{nl})}(\mathbf{r}, \mathbf{r}')$$

$$V_l^{(\text{nl})}(\mathbf{r}, \mathbf{r}') = \sum_{m=-l}^{+l} Y_{lm}(\hat{\mathbf{r}}) \sum_{j,k=1}^3 p_j^{(l)}(r) h_{jk}^l p_k^l(r') Y_{lm}^*(\hat{\mathbf{r}}'),$$

$$p_j^l(r) \propto r^{l+2(j-1)} \exp\left(-\frac{r^2}{(\sigma_l)}\right).$$

Goedecker, Teter and Hutter *Phys. Rev. B* **54**, 1703 (1996).

Dispersion calibrated atom centered potential

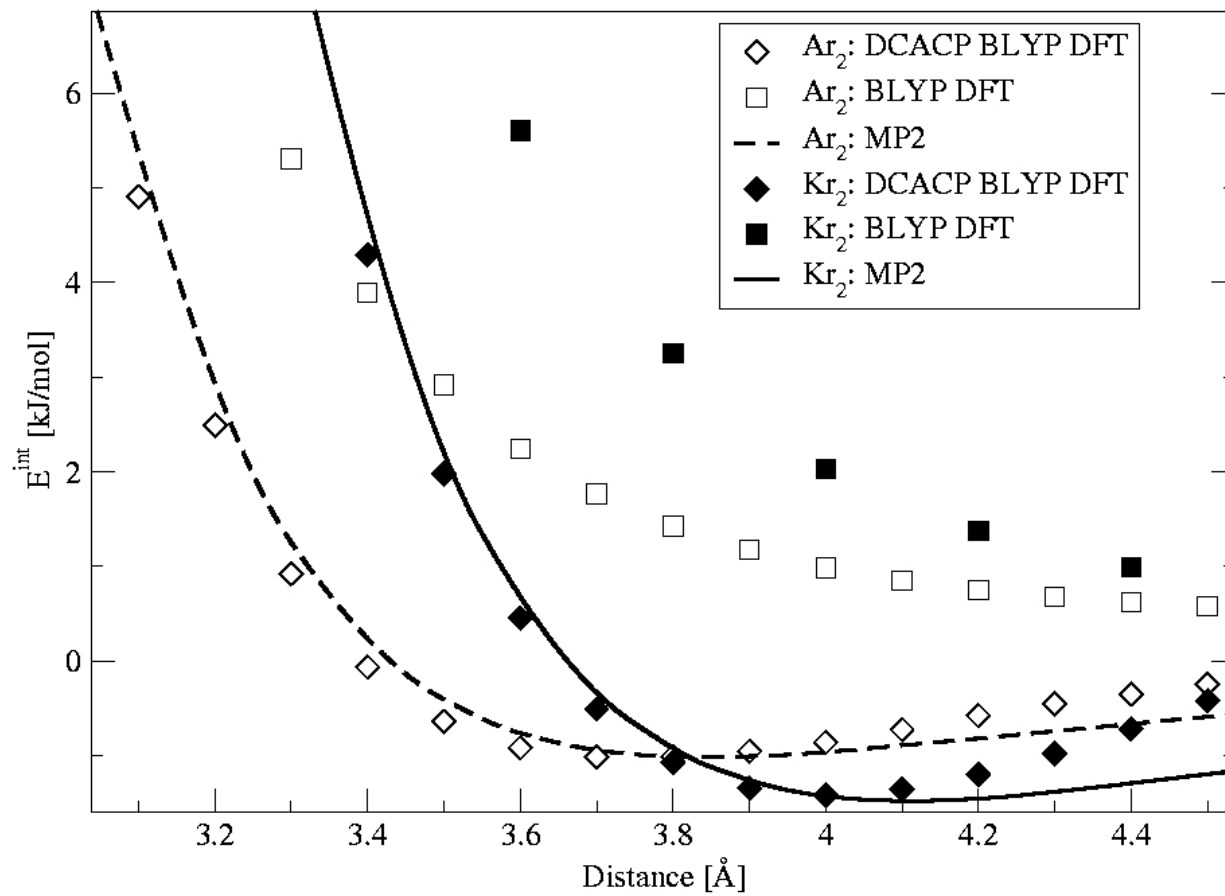
- Calibrate for an improved description of a molecular property:
e. g. for dispersion forces minimize

$$\mathcal{P}^{\text{disp}}(\mathbf{R}_{\text{ref}}) = (E_{\text{ref}}^{\text{int}}(\mathbf{R}_{\text{ref}}) - E^{\text{int}}(\mathbf{R}_{\text{ref}}))^2 + \sum_{\mathbf{I}} w_{\mathbf{I}} (\mathbf{F}_{\mathbf{I}}(\mathbf{R}_{\text{ref}}))^2$$

- For gradient based minimization one can use first order perturbation theory

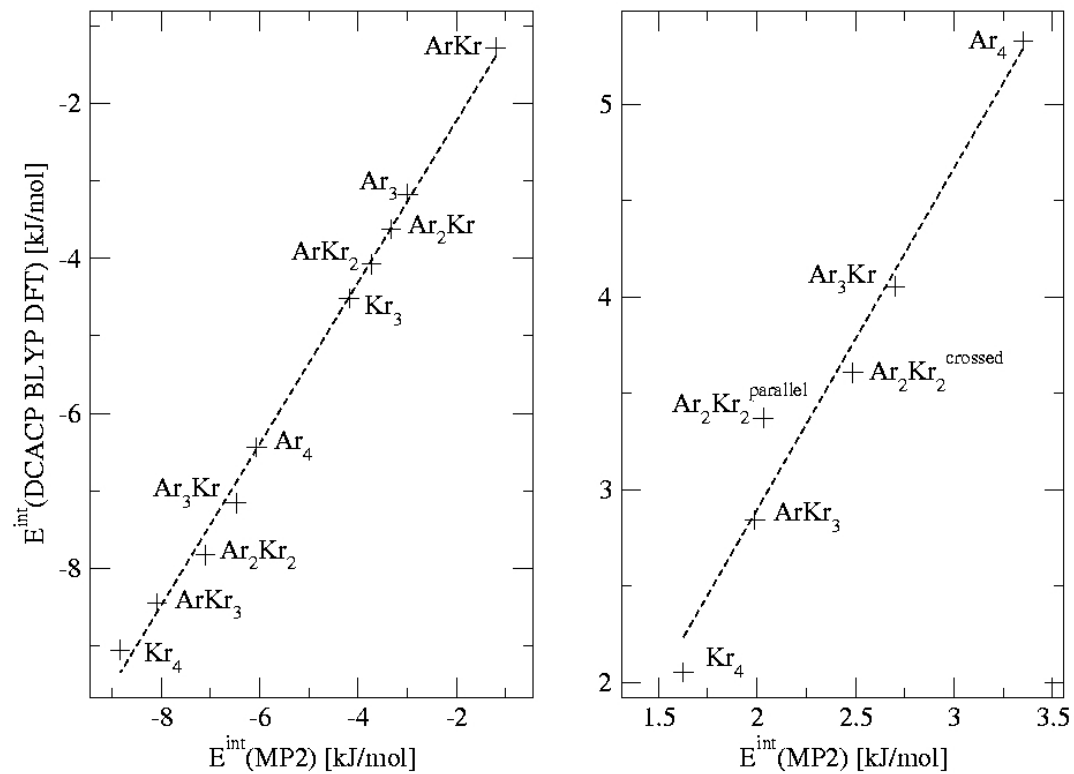
$$\begin{aligned} \frac{dE}{d\sigma_j} &= \langle \Psi | \frac{\partial \hat{H}}{\partial \sigma_j} | \Psi \rangle \\ &= \sum_i \langle \phi_i | \frac{\partial \hat{H}_i}{\partial \sigma_j} | \phi_i \rangle \end{aligned}$$

Example: rare gases



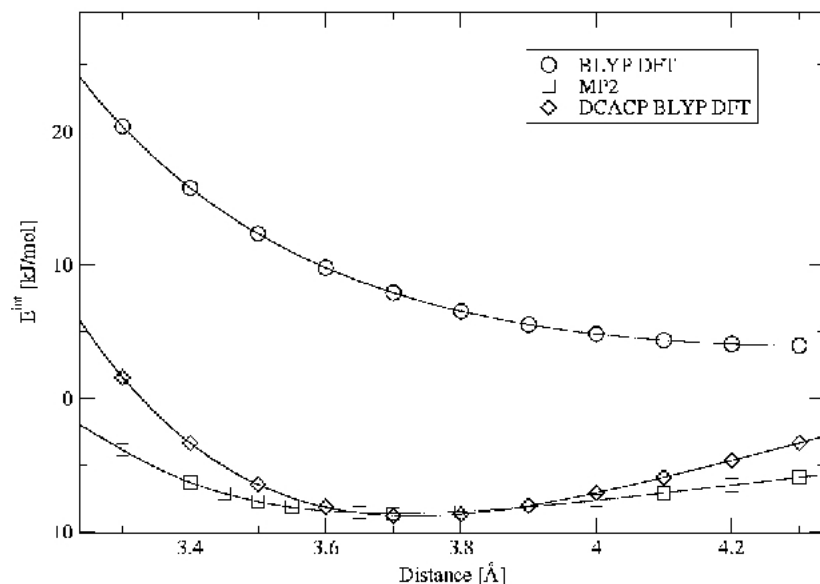
Transferability?

Equilibrium and barrier interaction energies for dimers, trimers, and tetramers



Interference with other intermolecular interactions?

Covalent bonds, permanent dipole moments, hydrogen bonding and dispersion: $(\text{Br}_2)_2$ and $(\text{HBr})_2$

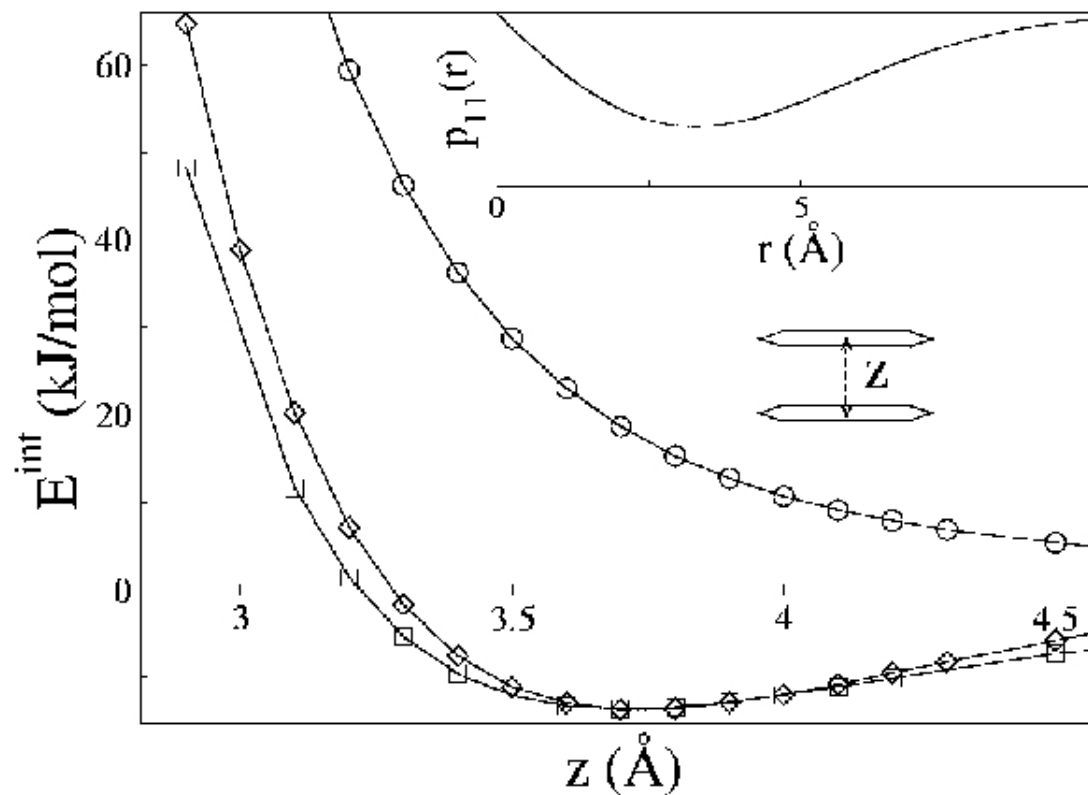


TS2: HBrBrH , TS3: HBrHBr

Deviation [kJ/mol] from MP2 reduces
from 4.2 to 0.3 for EQ, from 6.0 to 0.6 for TS1,
from 4.3 to 0.5 for TS2, from 4.3 to 1.2 for TS3.

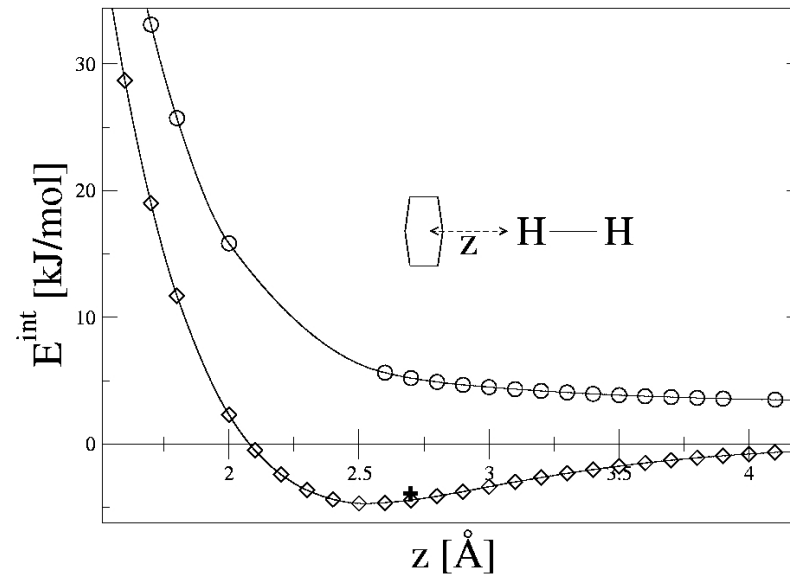
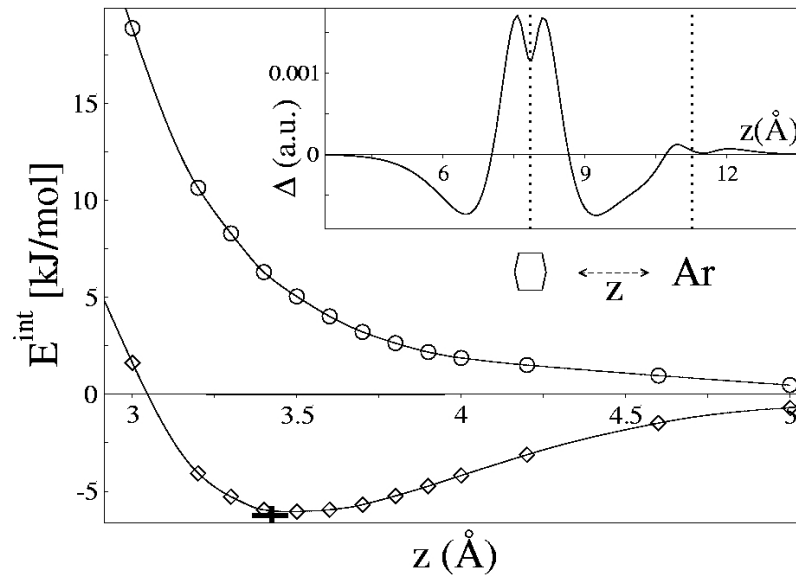
Carbon compounds: π - π -stacking

Calibration of carbon: the benzene sandwich



Assessing transferability

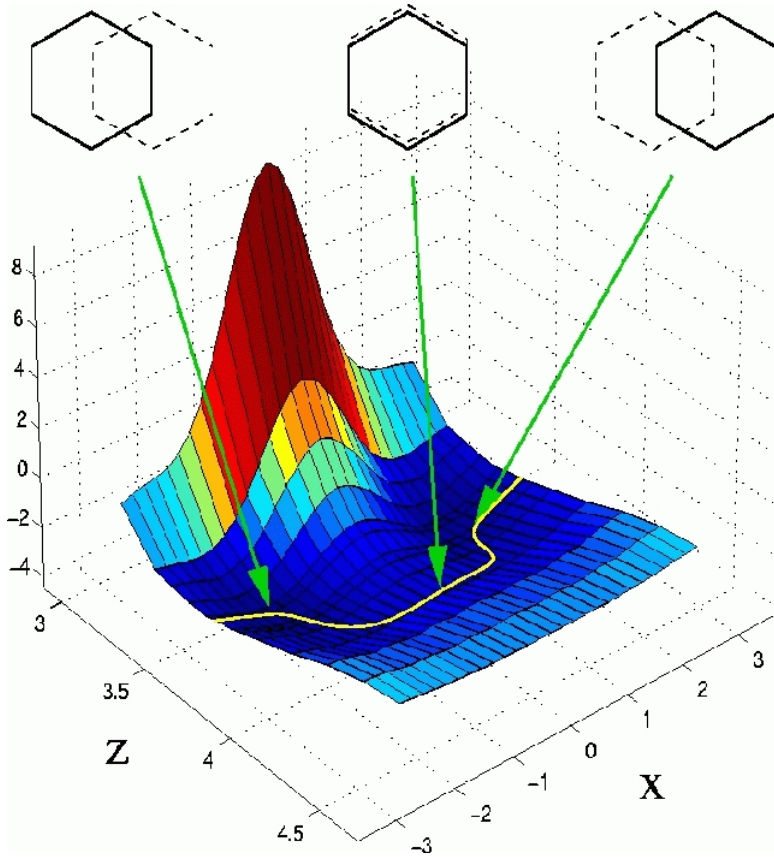
benzene-Ar, benzene-H₂



$$\Delta(z) = \int dx dy [n^{\text{BLYP}}(\mathbf{r}) - n^{\text{BLYP+DCACP}}(\mathbf{r})]$$

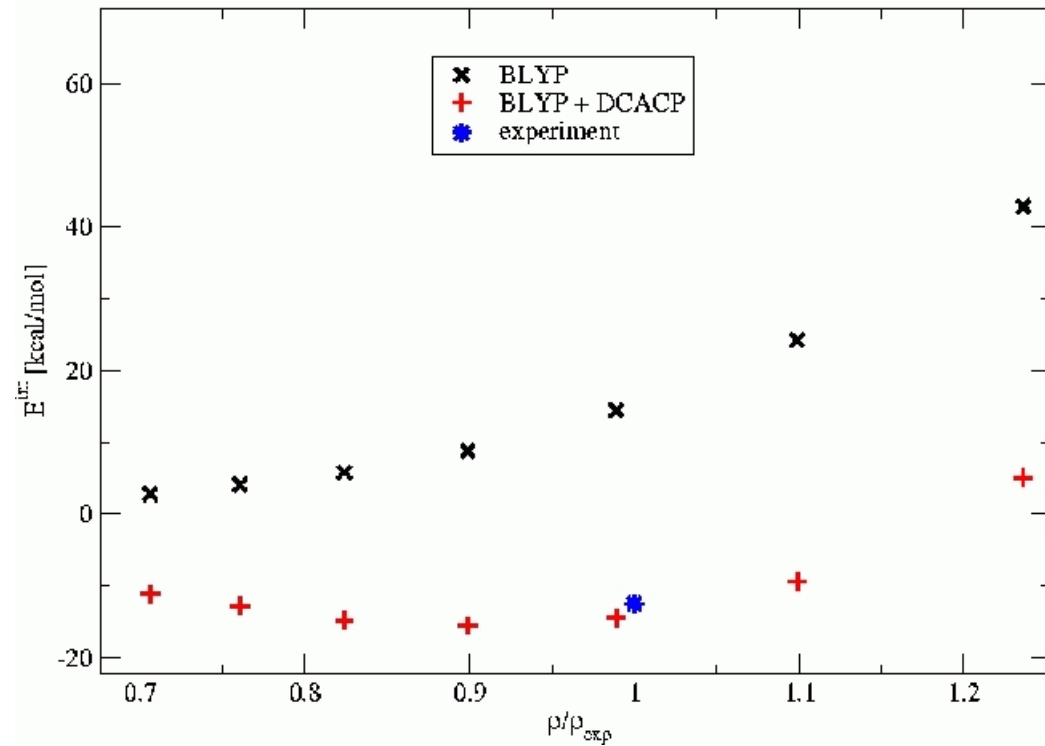
More carbon compounds

Benzene displacement, benzene crystal



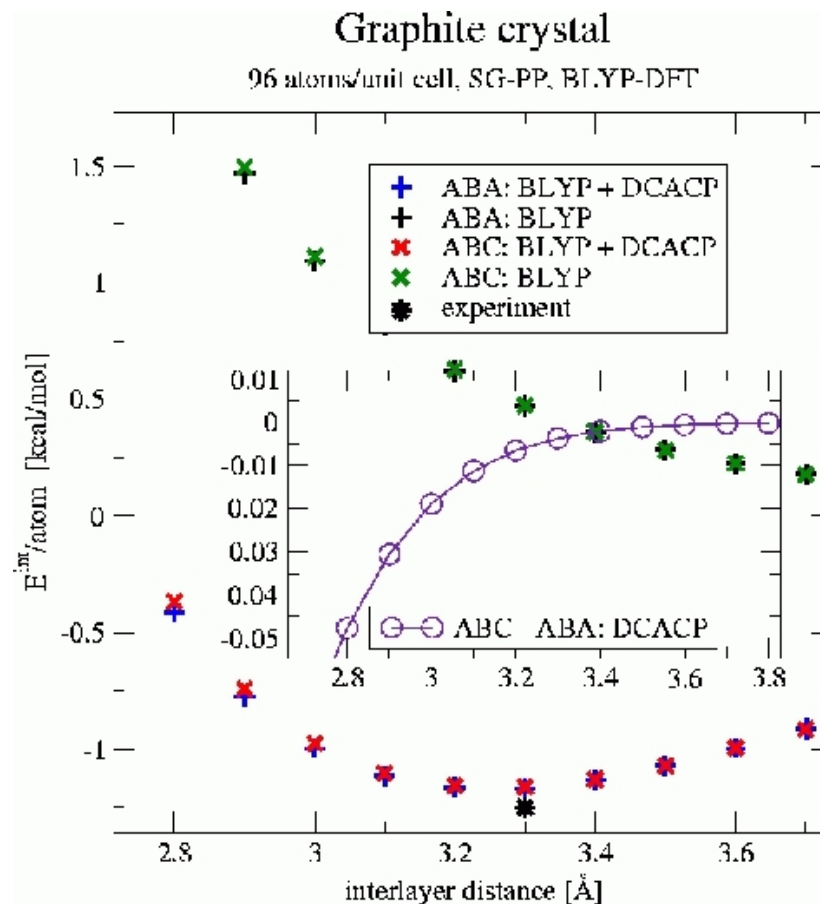
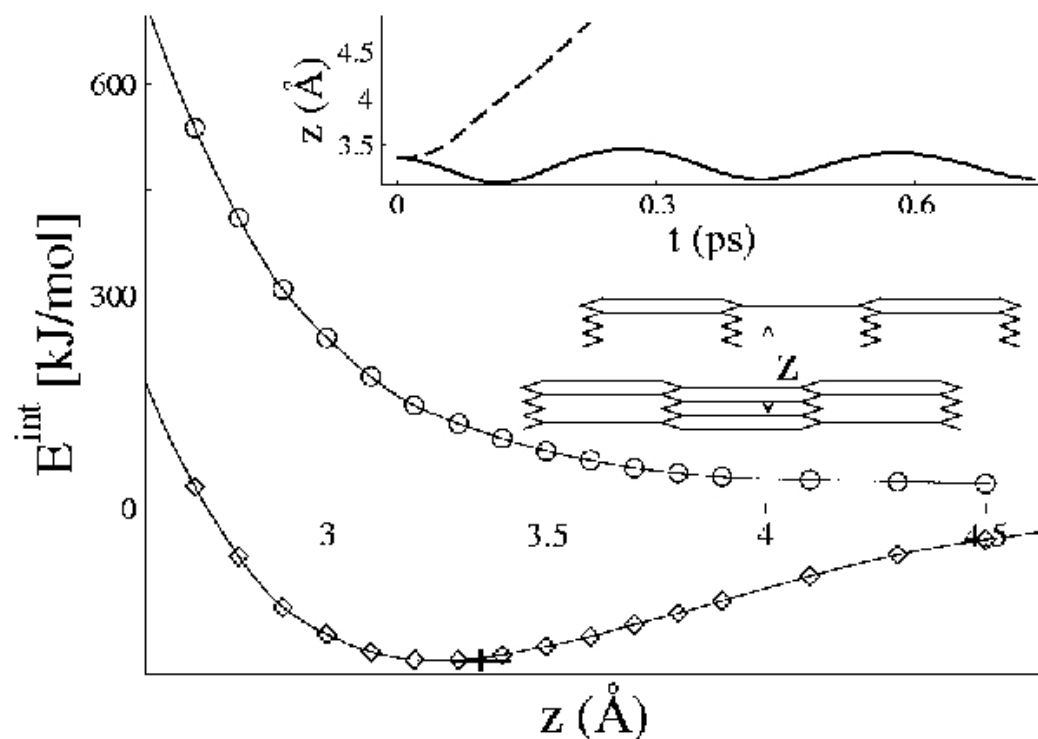
Cohesive energy of benzene crystal

P_{bsa} BLYP, SG-PP



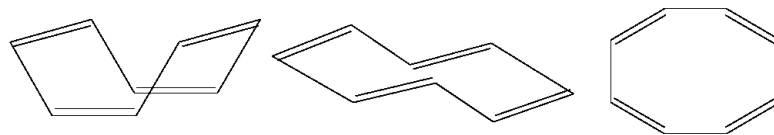
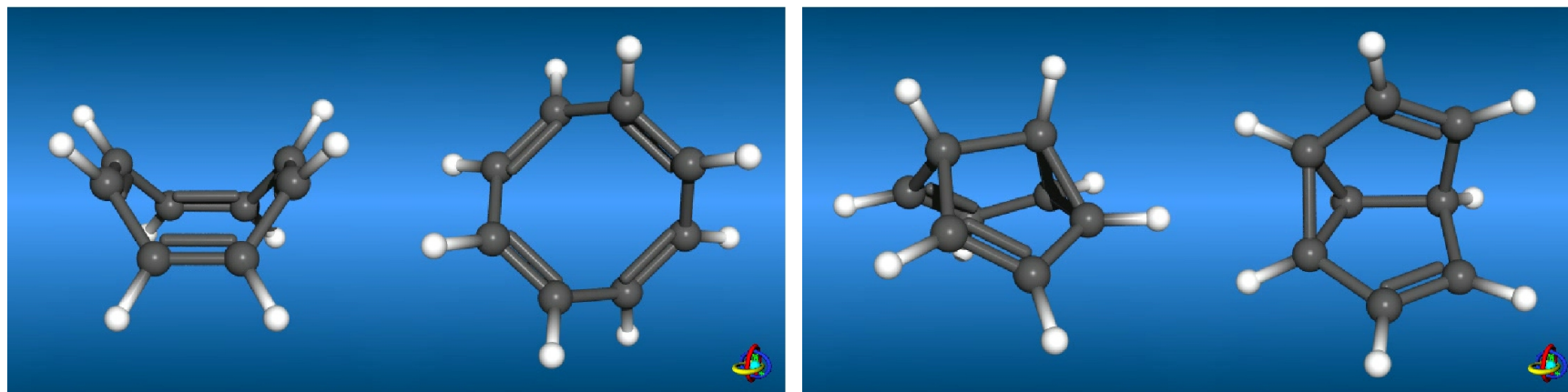
In periodic boundary conditions (PBC)

Graphene, graphite packing ABA vs ABC



Intramolecular interaction - conformation/folding

Cyclooctatetraene a precursor of semibullvalene



Barrier increases from 39.3 to 46.4 kJ/mol. Lit.: 45.6 - 57.1 kJ/mol.
Tub-Crown difference remains constant

Applications

- π -stacking in chemistry (solvents, metal complexes)
- π -stacking in biology (nucleic acids, aromatic amino acids)
- π -stacking in physics (surface adhesion, solid cohesion)
- example: H₂ storage in carbon nanotubes

Intermolecular forces in DFT: Summary

- care is needed for choice of v_{xc}
- assess v_{xc} for system, e.g. PBE smallest average error for solids, BLYP for isolated molecules...
- intermolecular interactions important? Use correction scheme for molecular dynamics in order to generate correct trajectory and thereby to sample phase space correctly.
- Bad example, adhesion of phenylalanine on surface...
- in CPMD 2 correction schemes are possible