Van-der-Waals Forces for Density Functional Theory Calculations

New project proposal for Schwerpunktprogramm 1145

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Motivation

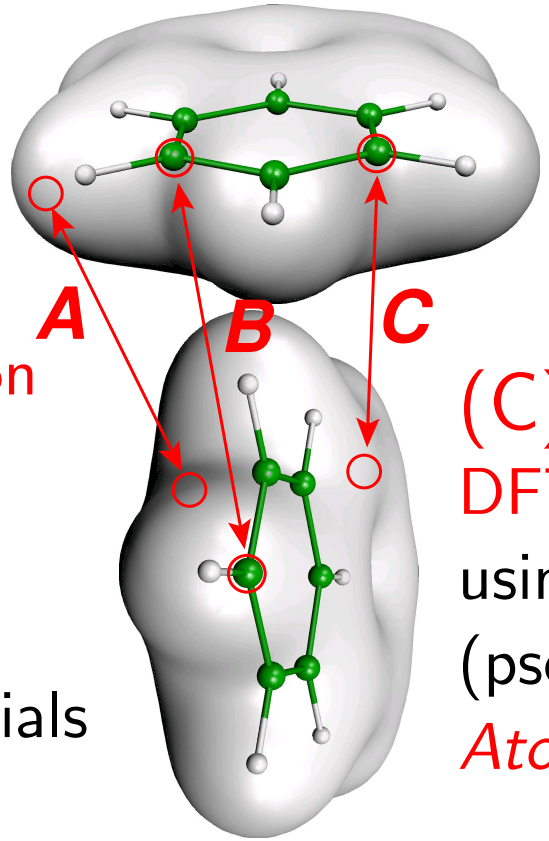
- Van-der-Waals interactions (London dispersion forces)
  weak but important
- "DFT = exact". . .
  But who has got the xc-functional? (...⟶ )
- LDA, GGA, hybrid functionals fail (sometimes fortuitous agreement)
  Accurate reference methods: CCSD(T), MP2,. . .
- Systematic correlated schemes *still* too expensive
  Molecular dynamics: gradient in $\Delta t \leq$1-2min required

$\Longrightarrow$ Pragmatic mixture between $\frac{C_6}{R_{ab}^6}$ and explicit correlation?

Preliminary work: Hybrid method

(A) Reference methods:
correlated levels of theory
(MP2, CC, . . .)
Electron–Electron interaction

(B) Empirical approach:
DFT + C_6/R_{ab}^6 pair potentials
Atom–Atom interaction



(C) Hybrid method:
DFT + OEPs
using non-local projectors
(pseudopotential style)
Atom–Electron interaction

Atom centered projectors

Nonlocal projectors in analogy to analytic pseudopotentials:

$$V_{\mathbf{R}}^{\mathrm{vdW}}(\mathbf{r},\mathbf{r}') = \sum_{m=-l}^{+l} \Phi_{lm}(\mathbf{r}-\mathbf{R})\; h_l\; \Phi_{lm}^{\star}(\mathbf{r}'-\mathbf{R})$$

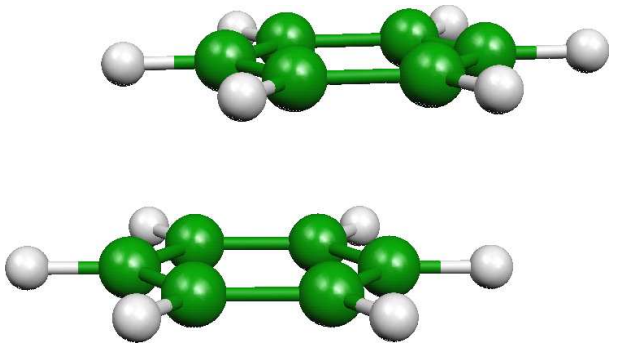
$$\Phi_{lm}(\mathbf{r}) \propto Y_{lm}(\mathbf{r})\; r^l\; \exp\left(-\frac{r^2}{2{\sigma_l}^2}\right)$$

Optimization of σ_l (widths) and h_l (amplitudes)
to achieve weak, attractive, long-ranged potential

Choice of l: first angular momentum channel that is not in pseudopotential

A. Lilienfeld, I. Tavernelli, U. Rothlisberger and D. Sebastiani,
PRL **93**, 153004 (2004) and *PRB* **71**, 195119 (2005)

Optimization of σ_l and h_l



Minimization of penalty functional:

(one specific system)

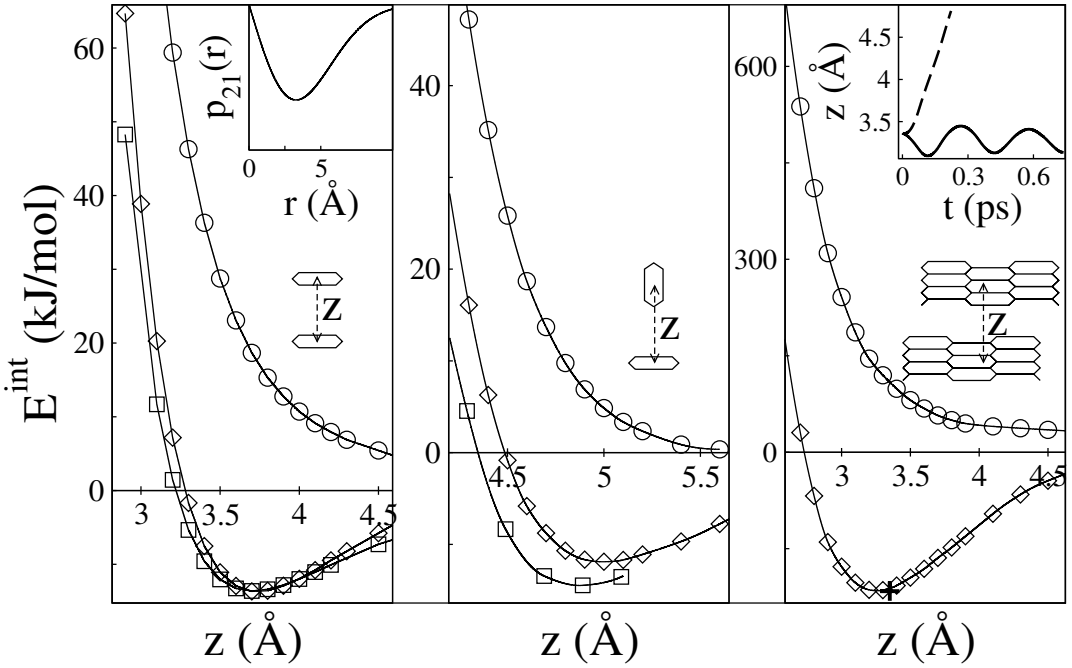
$$\mathcal{P}^{\text{disp}}(\sigma_l, h_l) = \left| E^{\text{ref}}(\mathbf{R}^{\text{ref}}) - E^{\text{DFT}}_{\sigma_l,h_l}(\mathbf{R}^{\text{ref}}) \right|^2 + \sum_I^{N_{\text{ions}}} w_I \left| \mathbf{F}^{\text{DFT}}_I(\mathbf{R}^{\text{ref}}) \right|^2$$

Quantifies deviation in depth and location
of potential energy minimum with respect to reference calculation

Reference calculation: MP2 or better ($E^{\text{ref}}(\mathbf{R}^{\text{ref}})$)

Reference configuration: Potential energy minimum ($\mathbf{F}^{\text{ref}}_I(\mathbf{R}^{\text{ref}}) = 0$)

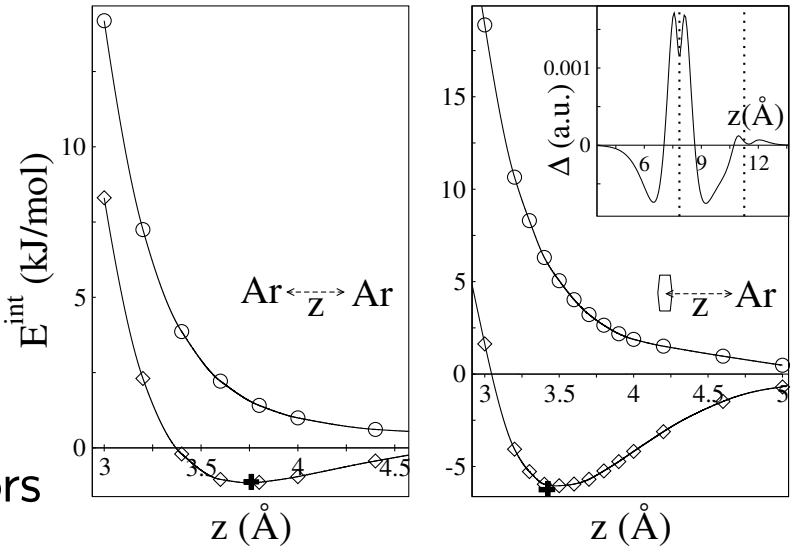
Preliminary results: Benzene, Argon



Argon$_2$: Calibration

Benzene–Argon complex:

Transferability check (OK)



Parallel (benzene)$_2$: Calibration of carbon projectors

T-shaped (benzene)$_2$: Transferability check (OK)

Graphite: Comparison with (experimental) equilibrium distance and energy (OK)

Solid state: Graphite $\rightarrow$ excellent layer distance

Benzene–Argon: Very good equilibrium distance

Proposed project

- Extensions: Further atom types

  Present stage: carbon, noble gases

  $\Longrightarrow$ New vdW-projectors for other systems

- Refinement: New functional forms

  Present functional form: motivated by simplicity of implementation

  $\Longrightarrow$ New projector types for V^{vdW}: Gaussian vs. exponential and algebraic

- Many-body-effects

  So far: only dimers/small oligomers investigated

  $\Longrightarrow$ Effects in supramolecular systems? Systems in the condensed phase?

- First real applications

  $\Longrightarrow$ Properties (NMR, IR, . . .): direct and through-geometry effects

  $\Longrightarrow$ Molecule–surface interactions: modification of adsorption properties

  $\Longrightarrow$ Car-Parrinello molecular dynamics simulations

Work Schedule