

# Coupling DFT with ab-initio – Test of quality

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**Presentation for the Praktikum in  
Theoretical Chemistry**

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# 1. Theoretical background

## Complementary of methods: advantages

- Ab initio
  - Good description of static (long range) correlation
  - Systematically improvable using larger basis sets  
=> high accuracy
- DFT
  - Dynamic correlation
  - Good cost-value ratio, weak basis-set dependence

# 1. Theoretical background

## Complementary of methods: disadvantages

- Ab initio
  - Problems with dynamical correlation, e.g. ee-cusp  
=> large basis sets required (expensive)
- DFT
  - Errors are not systematically
  - Results are not systematically improvable

# 1. Theoretical background

## Ansatz:

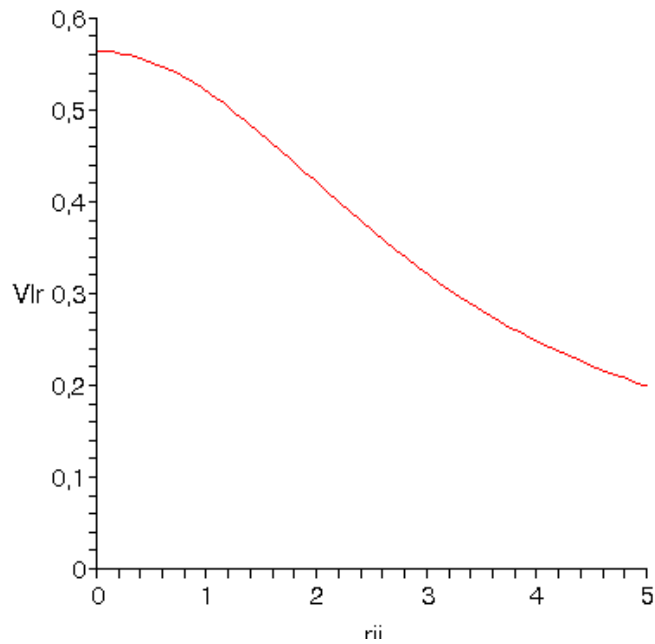
split  $\sum_{i<j} \frac{1}{r_{ij}}$  part of Hamiltonian  $\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \underbrace{\hat{V}_{\text{ee}}}_{\sum_{i<j} \frac{1}{r_{ij}}}$  into

long-range and short-range contributions:

$$\sum_{i<j} \frac{1}{r_{ij}} = \underbrace{\sum_{i<j} \frac{1}{r_{ij}} \text{erf}(\mu r_{ij})}_{V_{\text{lr}}} + \underbrace{\sum_{i<j} \frac{1 - \text{erf}(\mu r_{ij})}{r_{ij}}}_{V_{\text{sr}}}$$

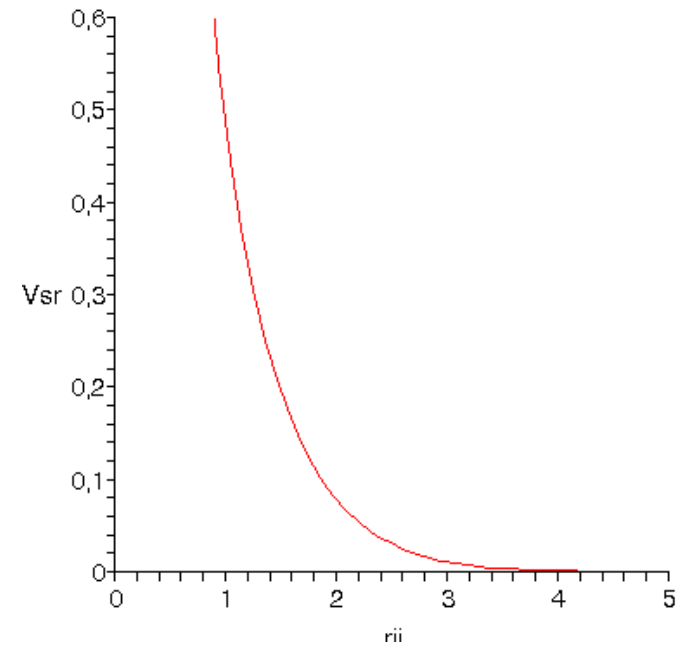
# 1. Theoretical background

b) Ansatz



Long-range part of  $1/r_{ij}$

$\mu=0.5$



Short-range part of  $1/r_{ij}$

# 1. Theoretical background

Using Levy's constrained search formalism:

$$E_0 = \min_{\rho \rightarrow N} \left( \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ne} + V_{ee}^{lr} | \Psi \rangle + E_0^{sr}[\rho] \right)$$

with

$$E_0^{sr}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ne} + V_{ee} | \Psi \rangle - \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ne} + V_{ee}^{lr} | \Psi \rangle$$

In  $E_0$ :  $V_{ne}$  cancel (only density dependent)

Classical Hartree terms  $U_{sr}$  can be extracted

Remainder (T and non-classical parts) are put into  $E_{xc}^{sr}[\rho]$

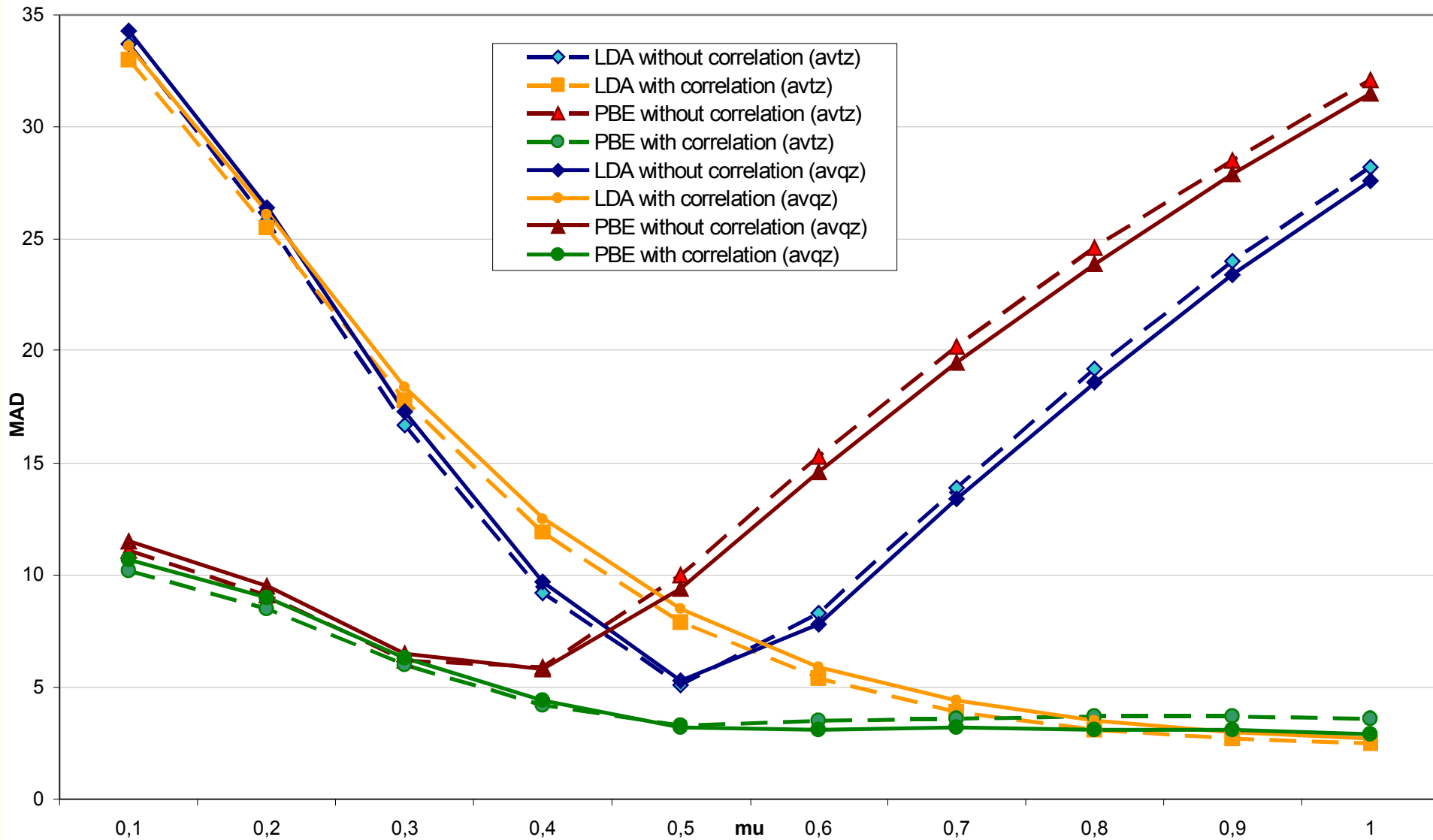
$$E_0^{sr}[\rho] = U_H^{sr}[\rho] + E_{xc}^{sr}[\rho]$$

$$E_0 = \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee}^{lr} | \Psi \rangle + U_{sr}[\rho] + \int v(r) \rho(r) dr + E_{xc}^{sr}[\rho]$$

# 1. Theoretical background

d) Long-range correlation

Mu-dependence/Effect of Ir-correlation (Atomisation energies)





# 1. Theoretical background

PBE exchange functional:

$$E_x^{\text{PBE, sr}}[\rho, \nabla \rho] = \int d^3 r \rho \epsilon_x^{\text{LDA}} F_x(\mathbf{s})$$

$$F_x(\mathbf{s}) = 1 + \kappa - \frac{\kappa}{1 + b s^2 / \kappa}$$

Changes:  $\epsilon_x^{\text{LDA}} \rightarrow \epsilon_x^{\text{LDA}}(\mu)$   
 $b \rightarrow b(\mu)$

- Recover gradient-expansion of sr exchange
- Borderline case  $\mu \rightarrow 0$ : transition to PBE

# 1. Theoretical background

PBE correlation functional:

$$E_c^{\text{PBE, sr}}[\rho, \nabla \rho] = \int d^3r \rho [\epsilon_c^{\text{LDA}} + H(r_s, t)]$$

$$H(r_s, t) = \gamma \log \left[ 1 + \frac{\beta t^2}{\gamma} \left( \frac{1 + At^2}{1 + At^2 + A^2 t^4} \right) \right]$$

$$A = \frac{\beta}{\gamma} \frac{1}{\exp(\epsilon_c^{\text{LDA}} / \gamma) - 1}$$

Changes:  $\epsilon_c^{\text{LDA}} \rightarrow \epsilon_x^{\text{LDA}}(\mu)$   
 $\beta \rightarrow \beta(\mu)$

- Correlation vanishes for rapidly varying gradients
- Damping out  $\beta$  for large  $\mu$

## 2. Practical performance

Need to test computational results  
and compare with „reality“ (experimental values)

Here: G2-Set as reference

- Well-established set of small test molecules
- Good experimental values available
- Contains different kinds of energy (AE, IP, EA, PA)
- Includes closed- and open-shell molecules

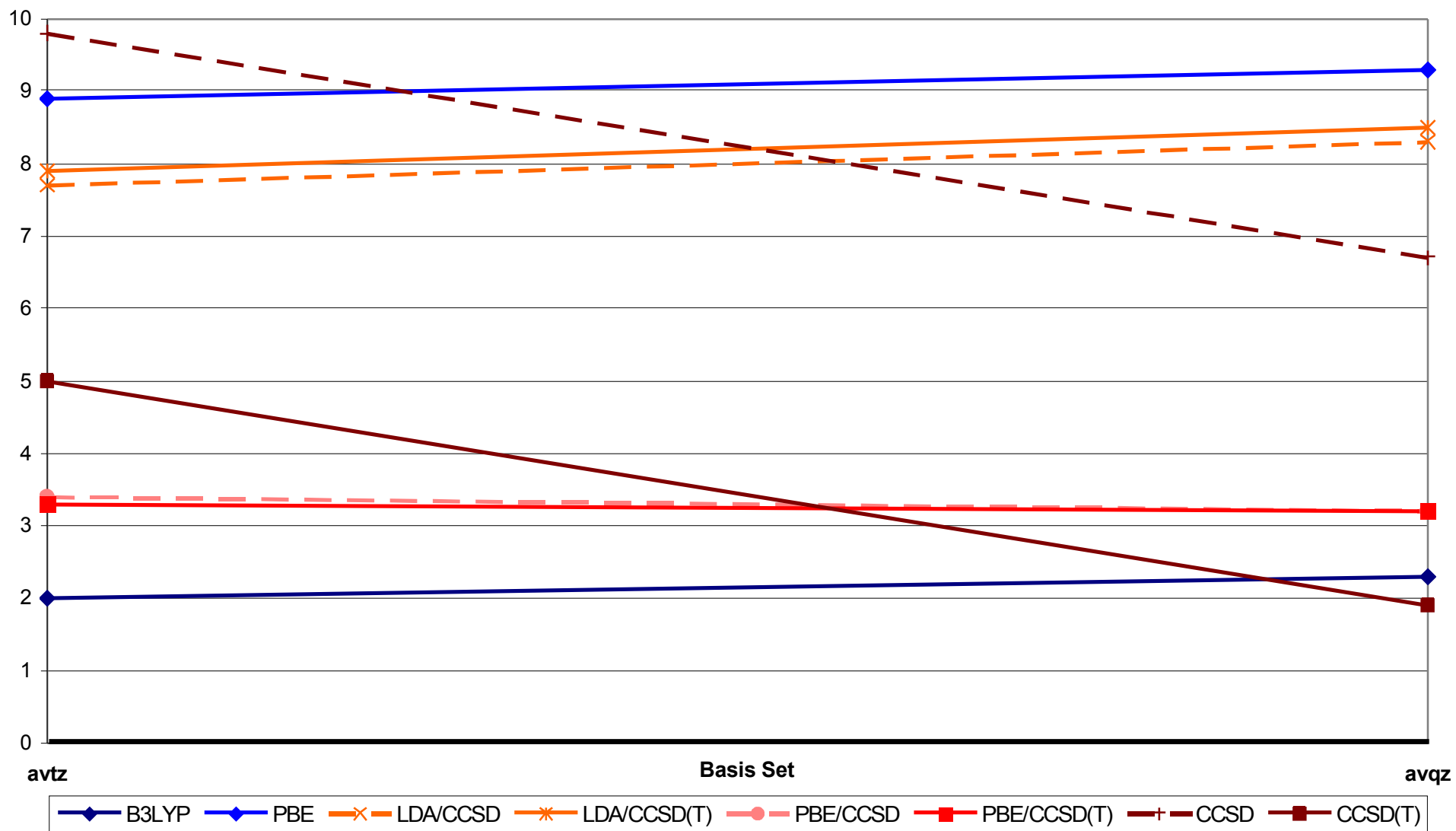
But:

- Only small molecules of mainly C,H,O,N (light elements),  
no transition elements
- Many molecules containing H

# 2. Practical performance

## (1) Dependence on basis set and functionals

MAD (kcal/mol) Basis set dependence (Atomisation energies)

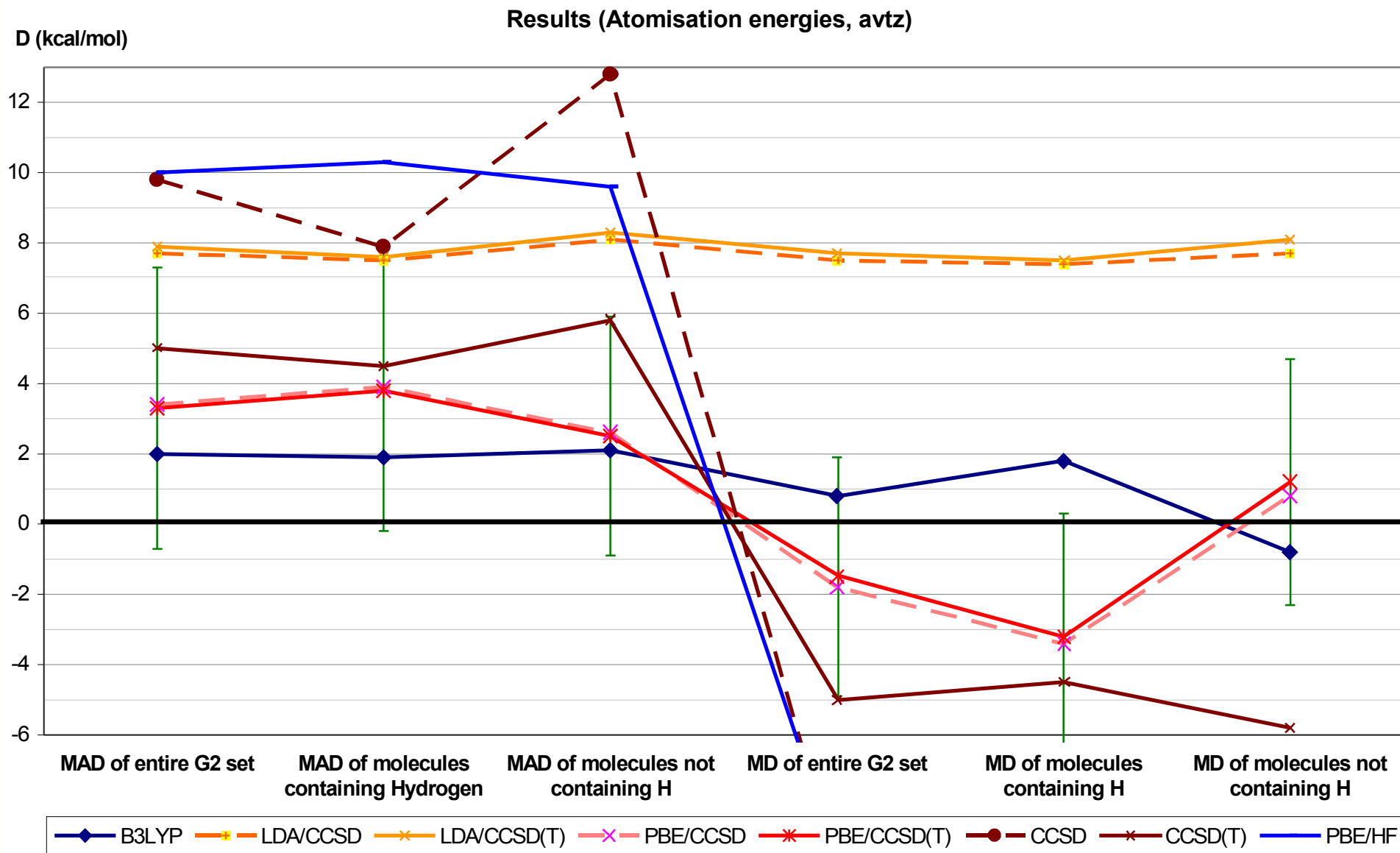


a) Results

# 2. Practical performance

## (2) Atomisation energies

a) Results



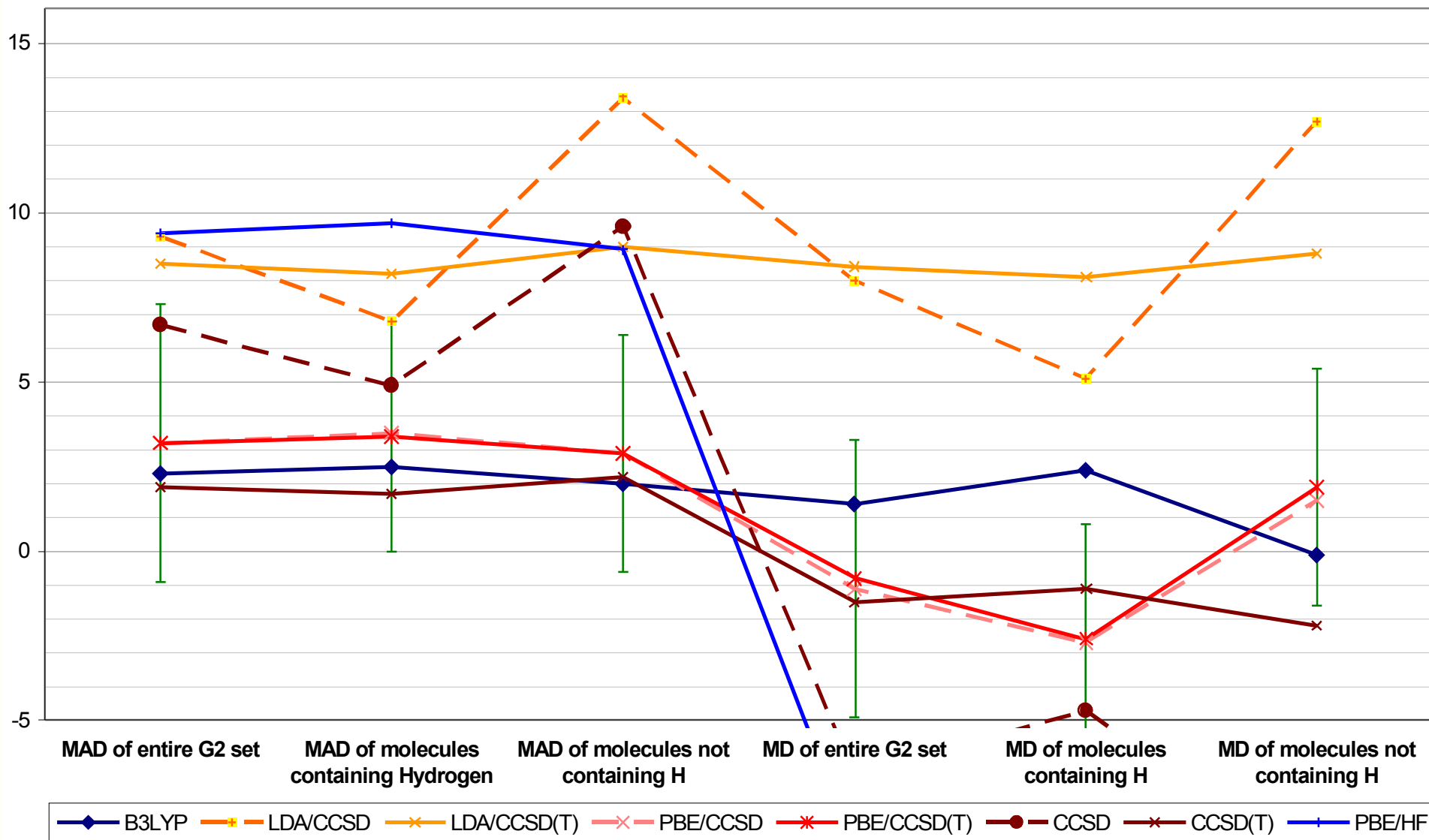
# 2. Practical performance

## (2) Atomisation energies

D (kcal/mol)

Results (Atomisation energies, avqz)

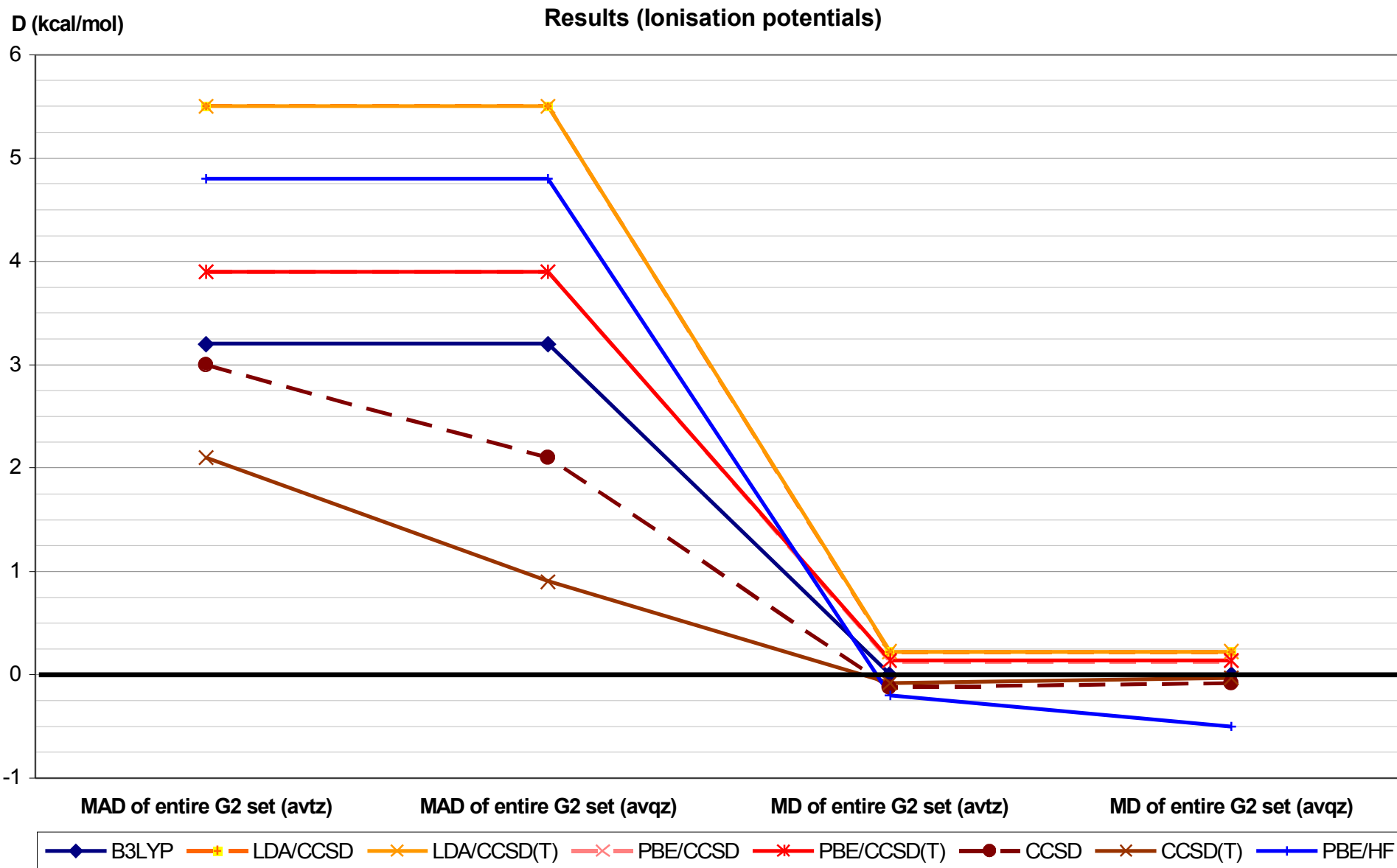
a) Results



# 2. Practical performance

## (3) Ionisation potentials

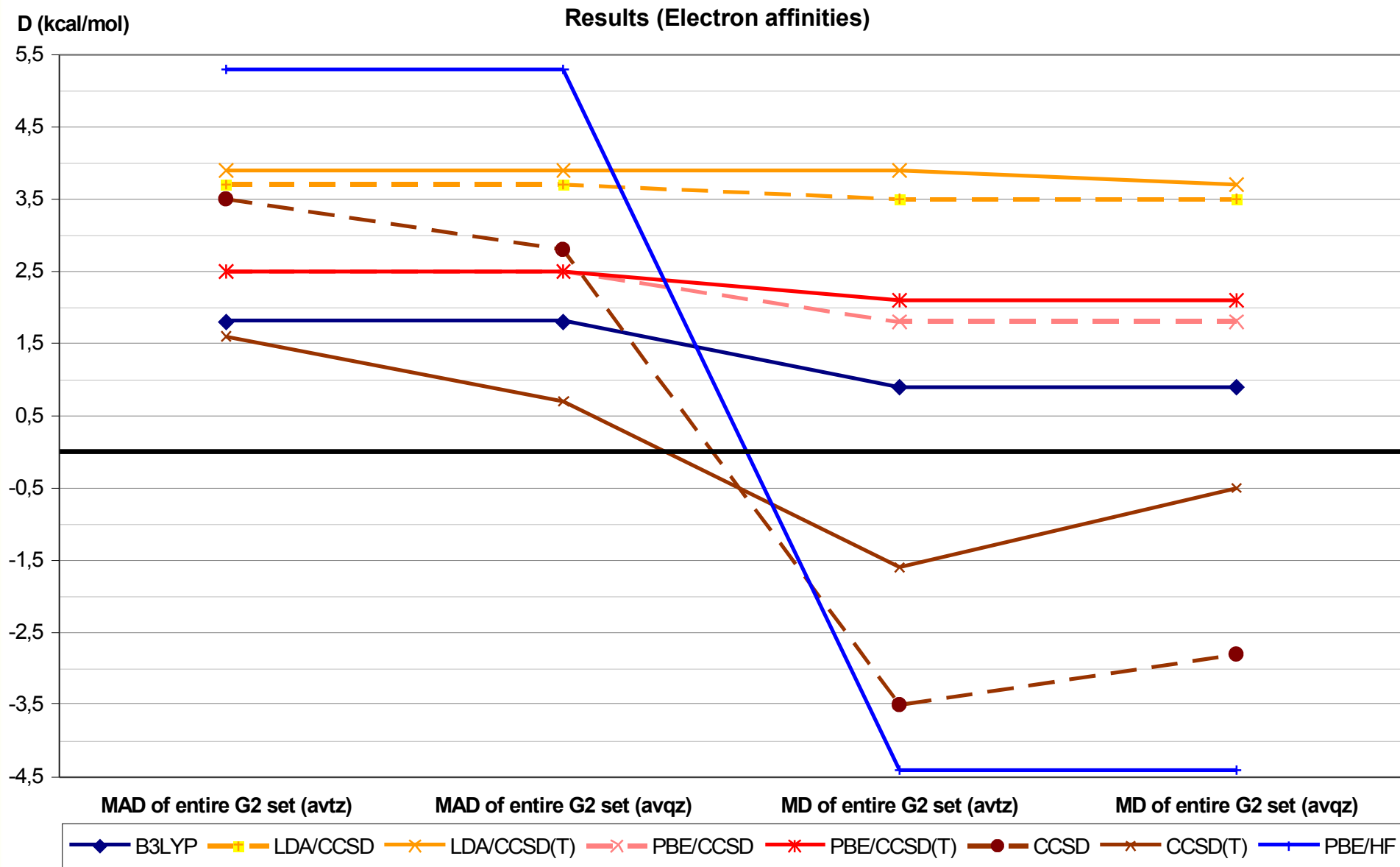
a) Results



# 2. Practical performance

## (4) Electron affinities

a) Results

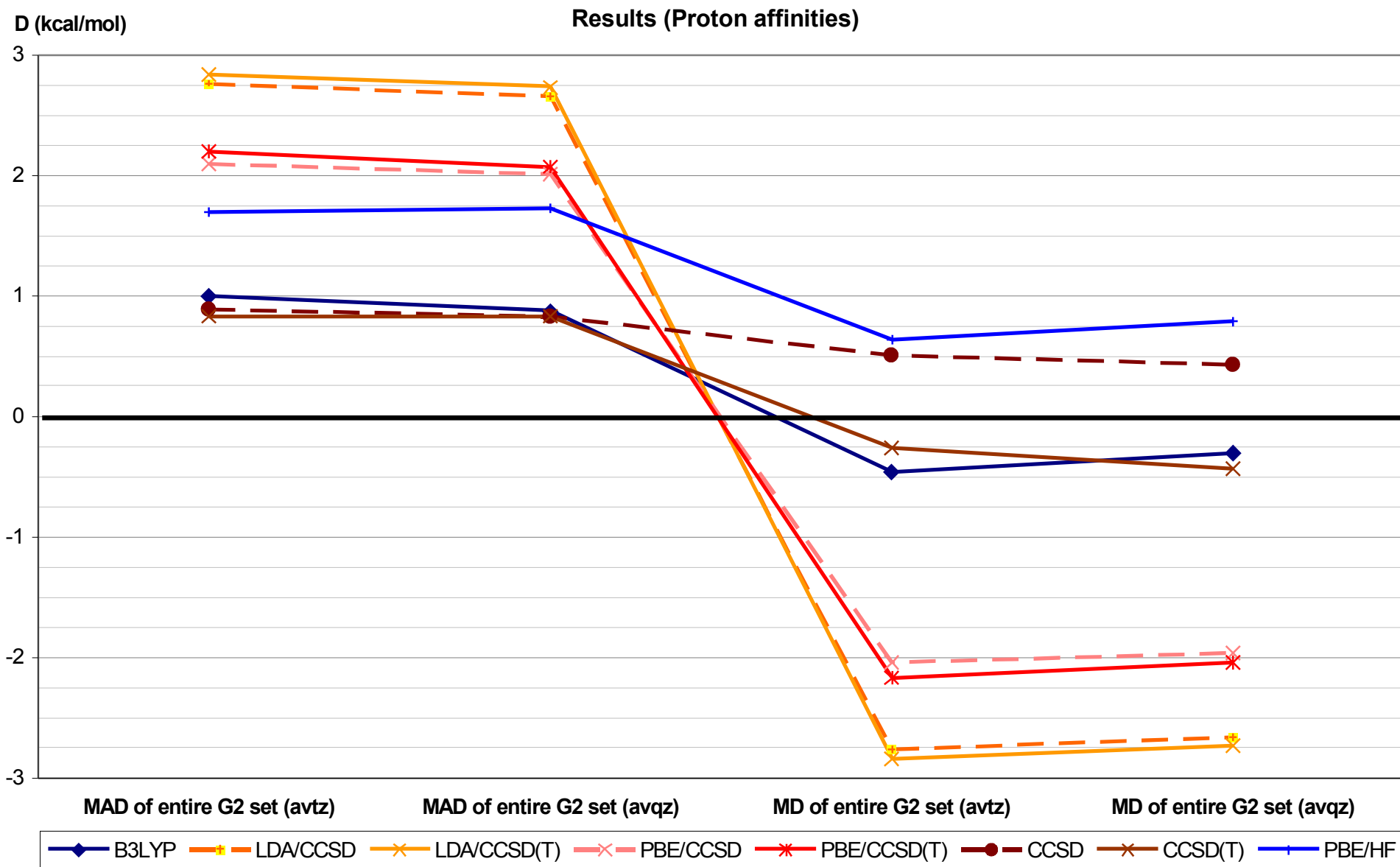




# 2. Practical performance

## (5) Proton affinities

a) Results



# 3. Conclusion & outlook

- Very encouraging results for atomisation energies (better than CCSD, almost as good as B3LYP)
- Not as good for rest, but:
  - ✓ MADs for entire G2-set ca. 2-4 kcal/mol (PBE/CC) (chemical accuracy almost, but not completely reached)
  - ✓ Triple excitation not very important
  - ✓ Only weak dependence on basis set
- Further steps:
  - Step upwards on „Jacob's ladder“: TPSS (better treatment of self-interaction)
  - Extend test set (more molecules, different elements)