



Conformational hierarchies of weakly-bonded systems: Accuracy of dispersion-corrected DFT

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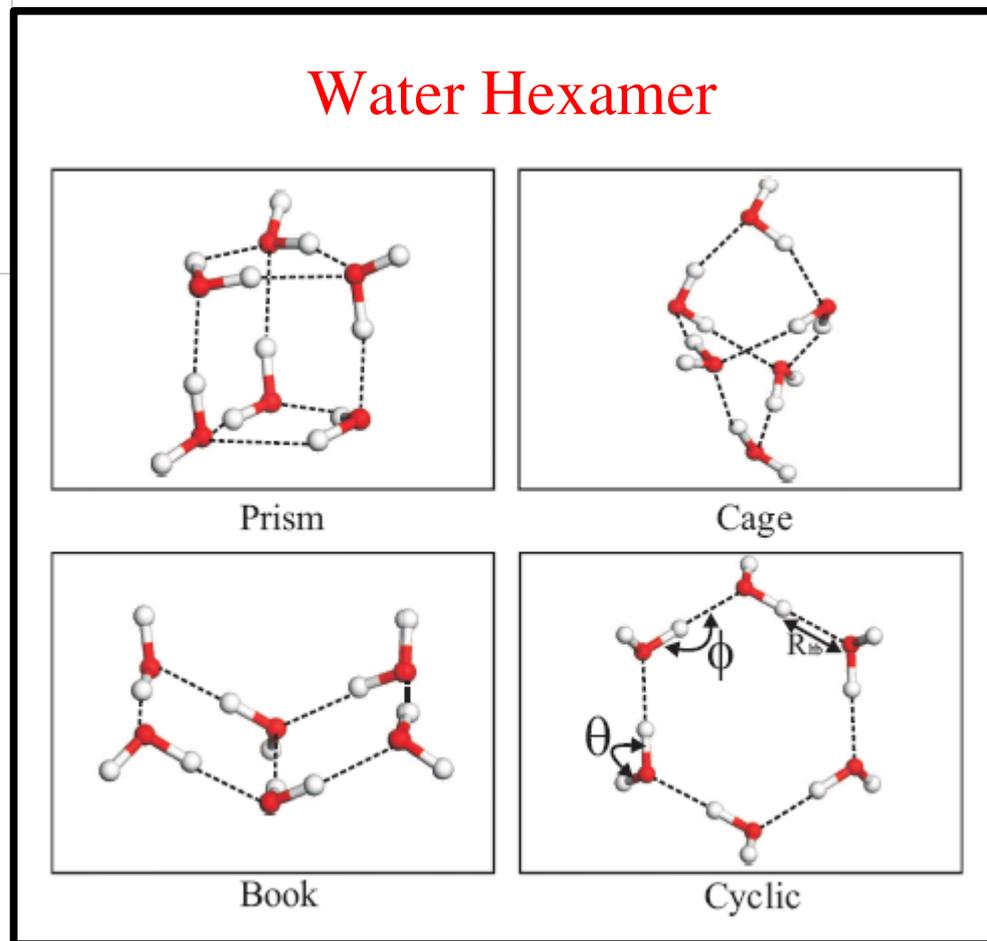
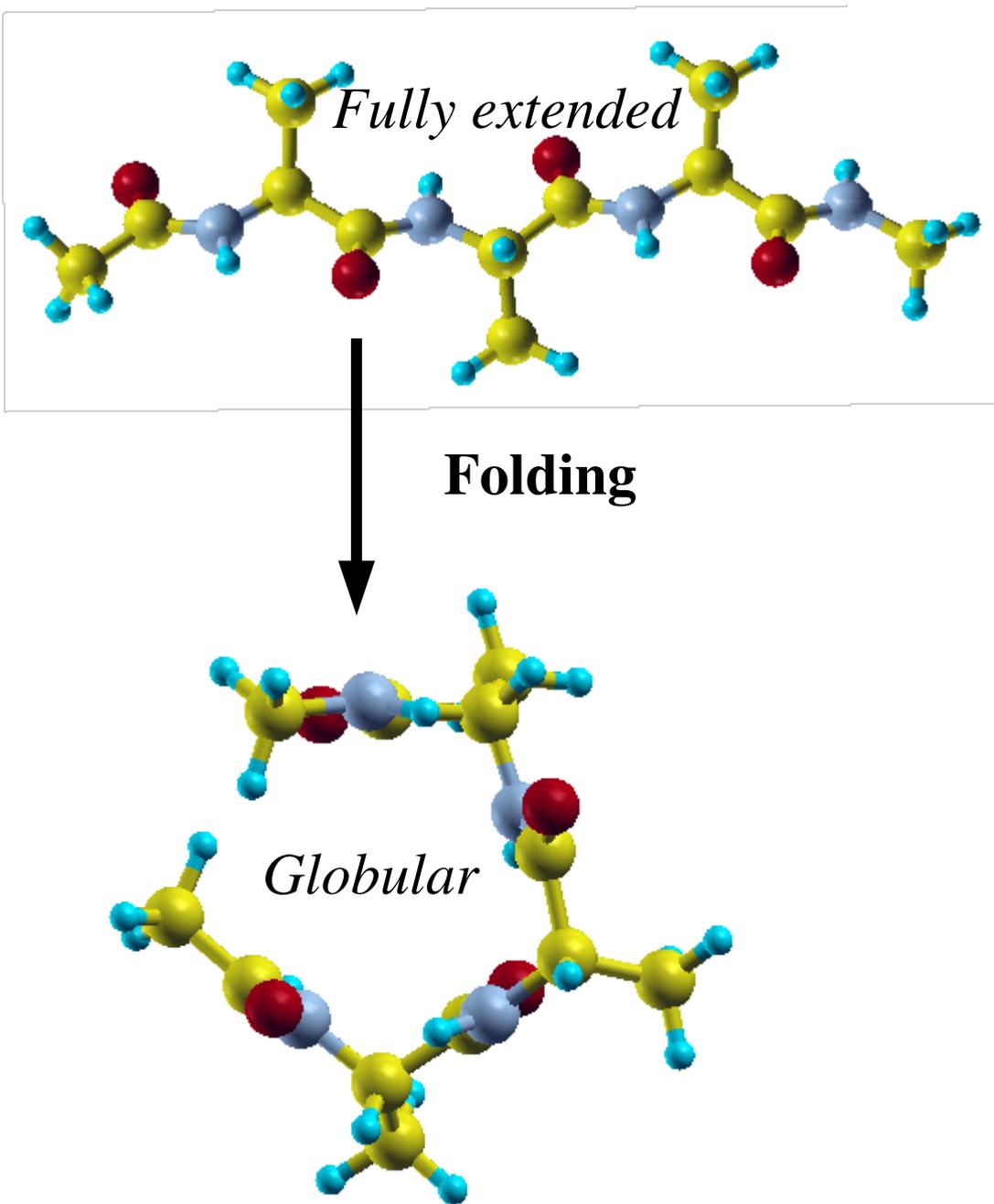
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Sandia Labs, NM, March 17, 2008

Conformational energy hierarchies

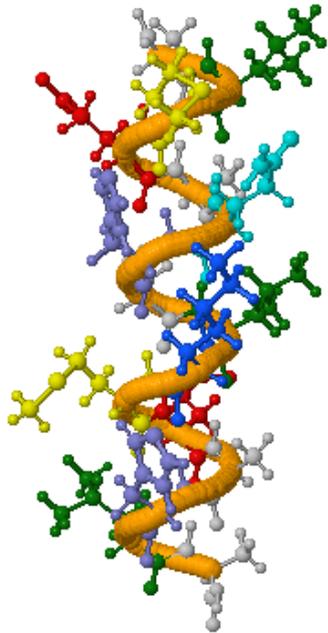


van der Waals (dispersion) forces

- **Attractive van der Waals forces** are ubiquitous, crucial for stability of molecular crystals, proteins or physisorption. They arise due to interaction between fluctuating dipoles (multipoles).



Gecko, wikipedia.org



Polypeptide helix

- State-of-the-art DFT functionals and Hartree-Fock theory **fail for description of van der Waals attraction**
- Post-HF methods can be employed for *ab initio* description of vdW interactions. Force fields include empirical vdW terms (Lennard-Jones).

Remedies for including vdW in DFT are abundant (C_6 corrections, non-local functionals (Langreth&Lundqvist), functional reparametrization, modified pseudopotentials, etc.)

Grimme J. Comp. Chem. (2004,2006); *Dion et al. PRL* (2004);
Zhao and Truhlar JCP (2006); *von Lilienfeld et al. PRL* (2004);
Johnson and Becke JCP (2005-2007); and many others ...

Motivation:

- 1) How important is the vdW correction for description of conformational energy hierarchies **COMPARED TO the present day xc functionals ?**
- 2) How much of the short-range vdW interaction **is already included in popular (semi)-local xc functionals ?**
- 3) **What is the best (accuracy AND feasibility) approach to include vdW interactions in DFT ?**

C_6 coefficients for DFT+vdW methods

For two non-overlapping spherical atoms:

$$E = -\left(\frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} + \dots\right)$$

- Accurate C_6 coefficients are tabulated for many elements. Must take care with different hybridization states though.
- *Becke&Johnson*: obtained “on the fly” from Hirschfeld partitioning
- *Langreth-Lundqvist functional*: does not need to determine them at all

	Error to QED(%)
United C6 per atom	10% - 20%
Becke first-principles	10% - 20%
Langreth-Lundqvist	10% - 20%

Damped $C_6 R^{-6}$ correction scheme*

Dispersion energy decaying as $C_6 R^{-6}$ is directly added to the DFT total energy, damped at short distances,

$$E_{dis} = -\sum_{ij} f_{damp}(r_{ij}, R_{ij}^0) C_{6ij} r_{ij}^{-6}$$
$$f_{damp} = \frac{1}{1 + \exp(-d(r_{ij}/R_{ij}^0) - 1))}$$

- Gradients are straightforward to implement
- The density is affected only due to changes in geometry
- C_6 coefficients taken from Wu & Yang (C, N, O, H atoms)
- Three parameters to be determined by a fit to post-HF data
- The fit is insensitive to the value of d . $d=20$ in what follows.

* Hepburn&Scoles CPL (1975); Elstner et al. JCP (2001); Wu, Yang JCP (2002); Grimme J. Comp. Chem. (2004,2006); Ortmann, Bechstedt, Schmidt PRB (2006); Jurecka, Cerny, Hobza, Salahub J. Comp. Chem. (2007); and others ...

Fitting to molecular database

- Fitting to *S22* database of Jurecka *et al.**
- 22 weakly-bonded systems, from pure dispersion (benzene dimer) to hydrogen bonding (water dimer)
- 20 meV – 0.8 eV binding energy span

*Jurecka, Sponer, Cerny and Hobza, *PCCP* (2006)

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Method	S_R	S_6	Std.Dev. (meV)	Ave % Error
HF	0.96	1.26	43	13.8%
PBE	1.00	1.00	24	11.1%
revPBE	0.76	1.24	25	9.6%
PBE0	1.04	1.00	30	9.5%
BLYP	0.87	1.33	13	4.3%
B3LYP	0.94	1.19	19	6.8%

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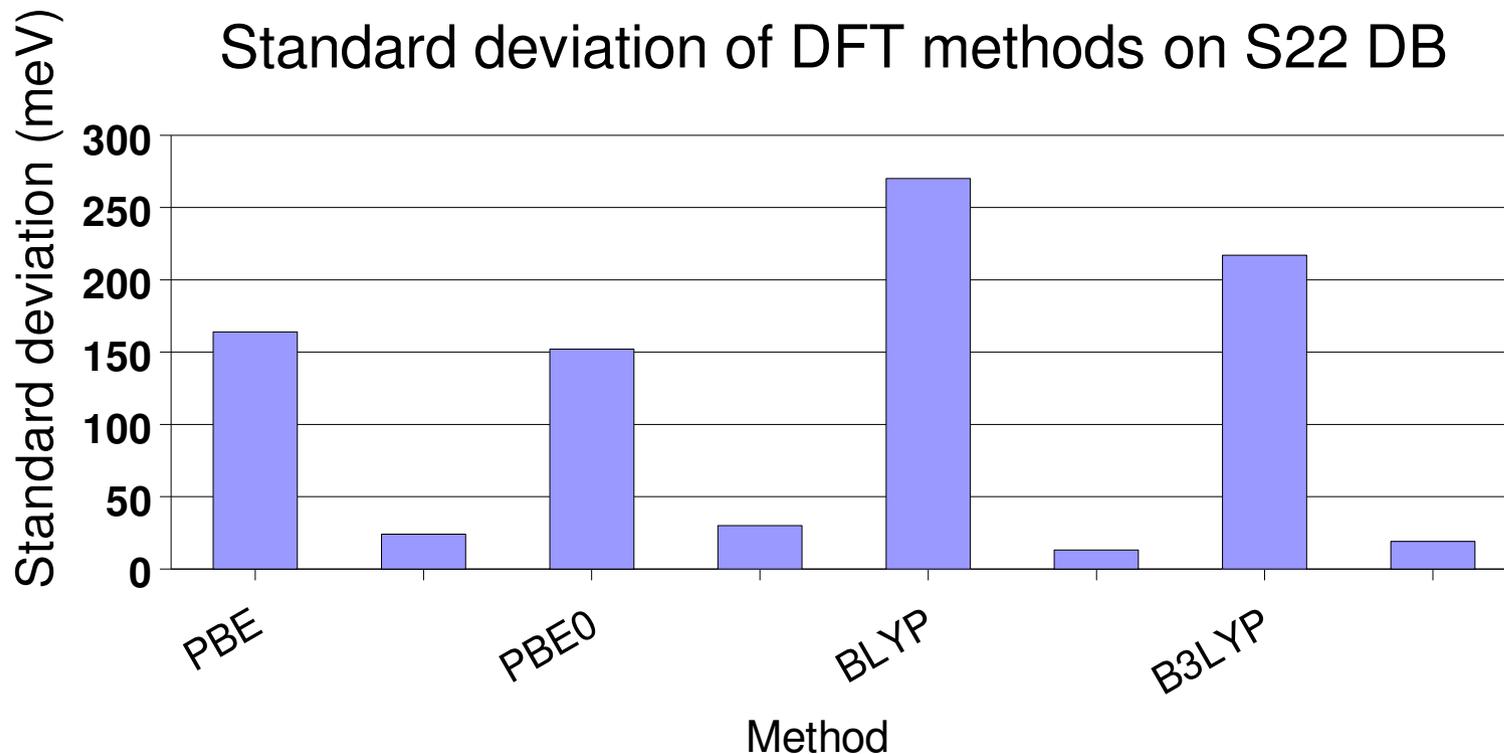
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- Hartree-Fock method is the worst, no short-range vdW
- revPBE, BLYP and B3LYP give lower errors, but require unphysical parameter values

• PBE and PBE0 are the most physically correct functionals for the dispersion correction

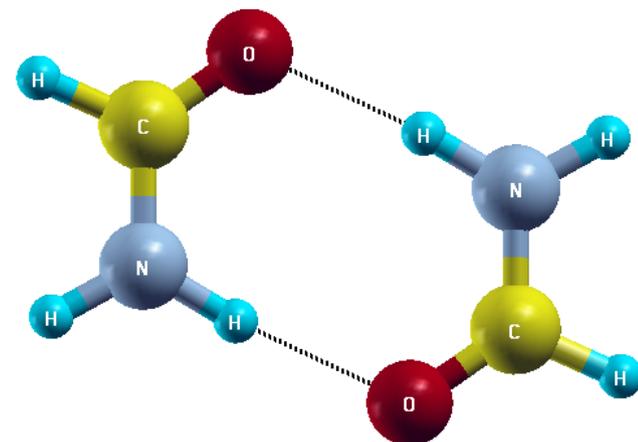
Corrected vs. uncorrected functionals



- The C_6 correction reduces the error 6-fold for PBE
- Short-range van der Waals interaction is better described by PBE and PBE0

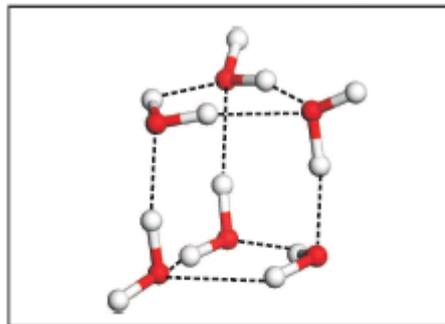
Numerical precision of DFT implementations

Conformer	NAO	Gaussians	Plane waves
FM1	-14.33 (-14.20)	-14.29 (-14.21)	-14.17
FM2	-9.07	-9.04	-8.99
FM3	-6.59 (-6.44)	-6.49 (-6.44)	-6.41
FM4	-6.25	-6.17	-6.12
FM5	-3.83	-3.80	-3.80
NMA1	-15.09	-15.08	-14.96
NMA2	-8.71	-8.69	-8.62
NMA3	-6.30	-6.30	-6.27
NMA4	-8.03	-8.05	-7.97

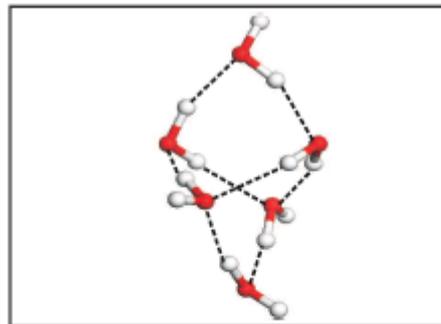


Test case: Water hexamer

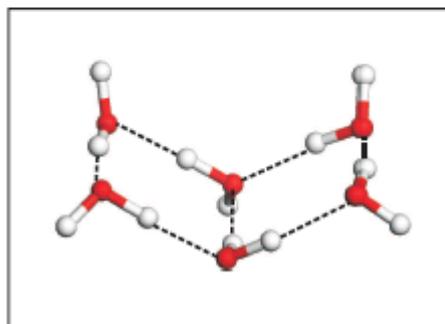
PRISM



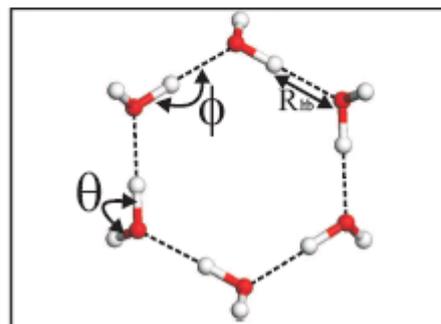
CAGE



BOOK



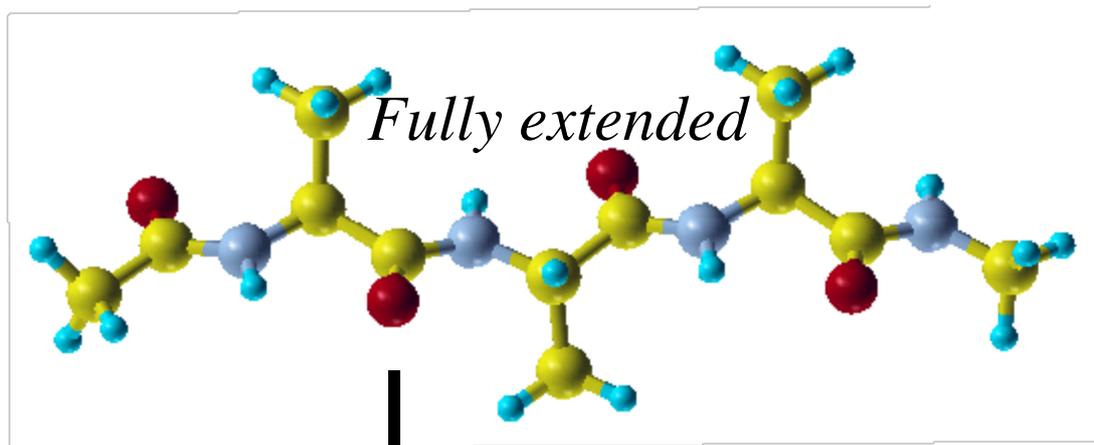
CYCLIC



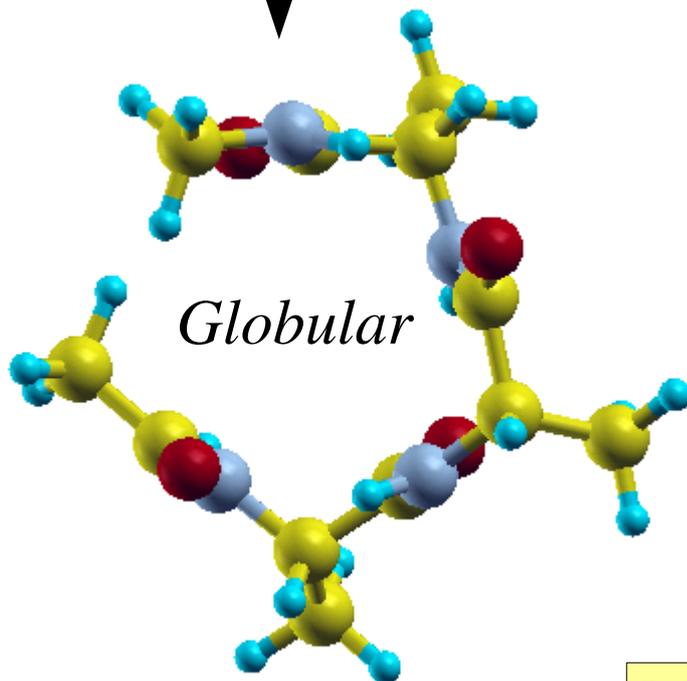
Binding energy / H₂O (meV)

	Prism	Cage	Book	Cyclic
MP2	332.7	331.1	330.4	322.9
PBE	336.1	339.4	345.5	344.1
PBE0	322.9	325.3	330.9	330.7
BLYP	272.1	276.0	286.7	289.7
PBE+C6	377.8	377.8	377.3	367.3
PBE0+C6	358.5	358.0	356.3	350.6
BLYP+C6	351.3	351.3	349.0	339.6

Alanine Tetrapeptide (Ala_4)



Folding



Fully relaxed geometries

CBS-MP2 energy: 216 meV

PBE energy: 2 meV

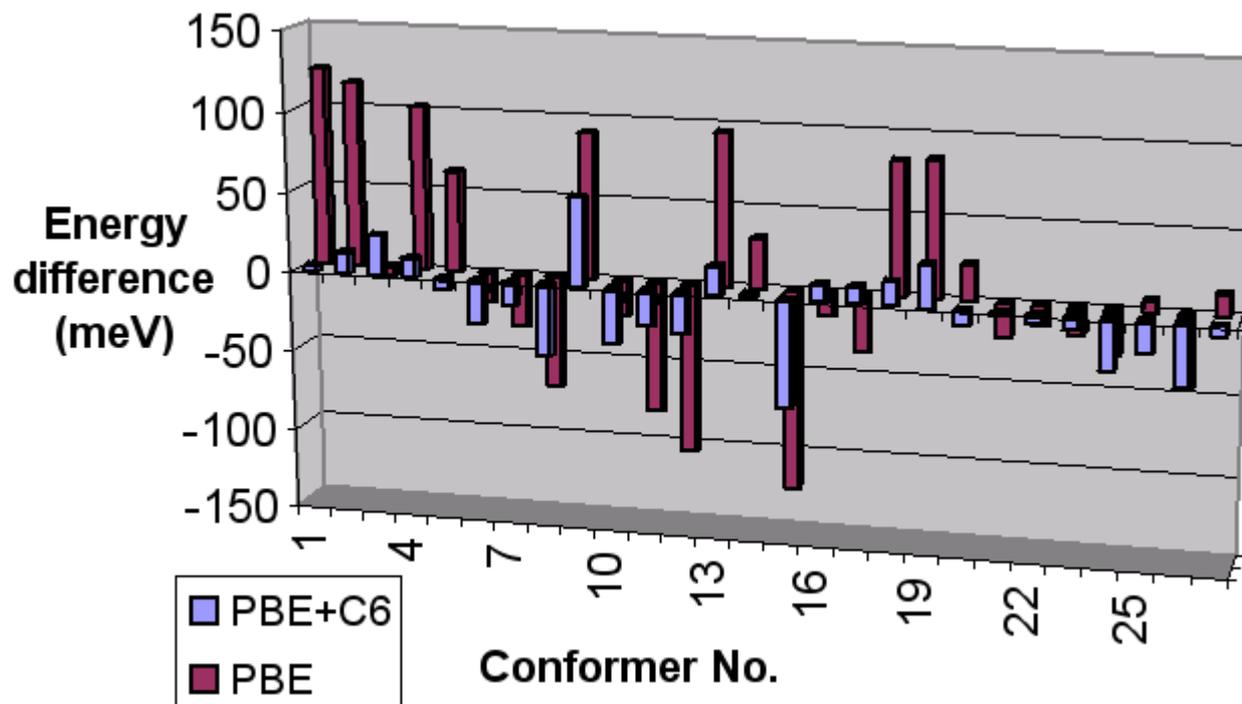
PBE+C6 energy: 220 meV

Alanine Tetrapeptide (27 conformers)

DFT-MP2 Error in meV

	Mean. abs error	Max error
PBE	54	123
PBE+C ₆	20	67
BLYP	77	185
BLYP+C ₆	35	113
PBE0	52	151
PBE0+C ₆	23	50

DFT-MP2 energy



Only 5 meV error per residue
with PBE+C₆ and PBE0+C₆

Folding energetics from first-principles: Polyalanine helices



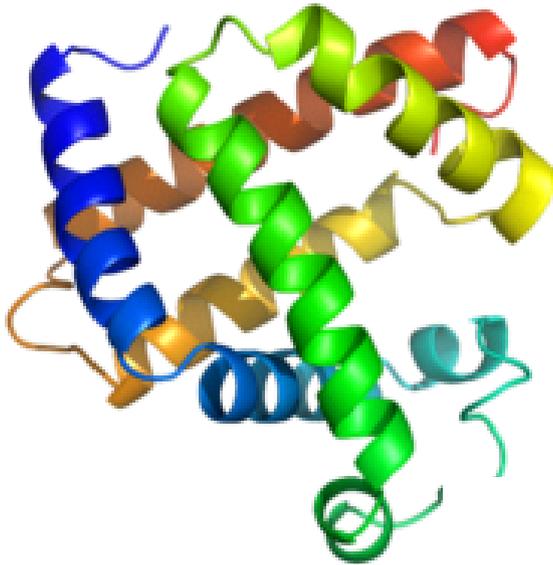
Myoglobin protein, wikipedia.org

Basic (and hitherto unanswered) Puzzle:

How stable are the
(poly)-Alanine helices *in vacuo* ?

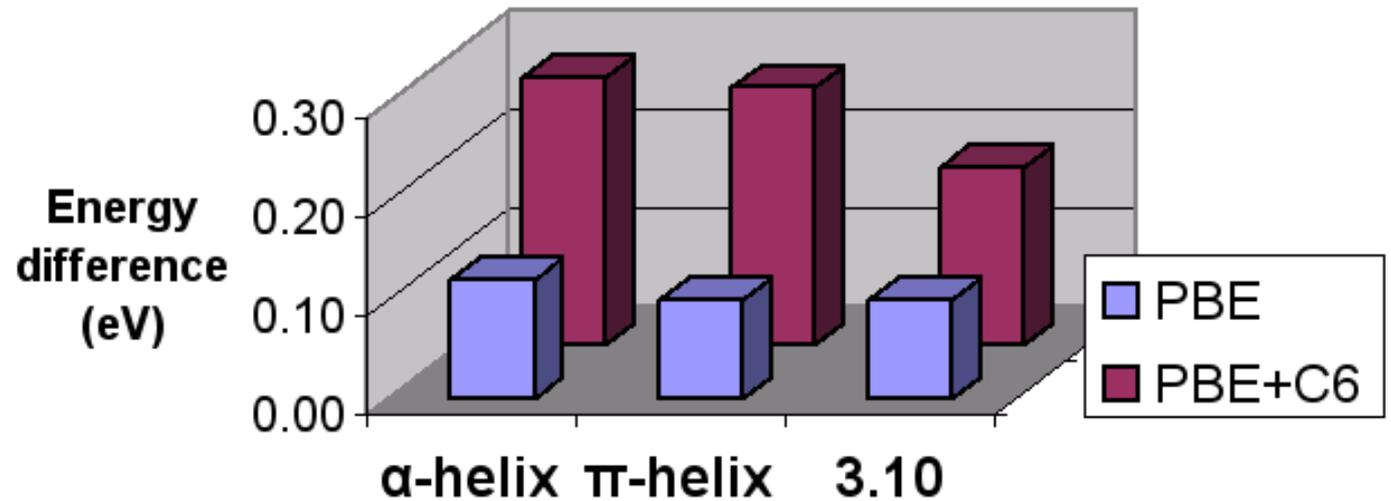
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Myoglobin protein, wikipedia.org



How stable are the (poly)-Alanine helices *in vacuo* ?

HELIX-FES stability (per residue)



C6 vdW contributions: 0.32 0.33 0.26 eV

Summary

- The van der Waals contribution to conformational energy hierarchies of weakly-bonded systems is strong (**it amounts to ~0.3 eV per residue for an infinite alanine α -helix using DFT-PBE !**)
- **PBE and PBE0 functionals represent the best alternative** for the *C6* correction. Short-range vdW interaction is described better.
- Comparison to published results for different systems favors the *C6* correction as one of the **most accurate and feasible approaches** for the time being
- Our *C6* correction parameters are transferable to any DFT code, since they were fitted close to the basis set limit



Acknowledgements

- Dr. Joel Ireta
- **FHI-aims** code team
- Members of the FHI theory department for enlightening discussions !

- Funding:

