

Applications of the van der Waals density functional: DNA and metal organic framework materials

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Chalmers



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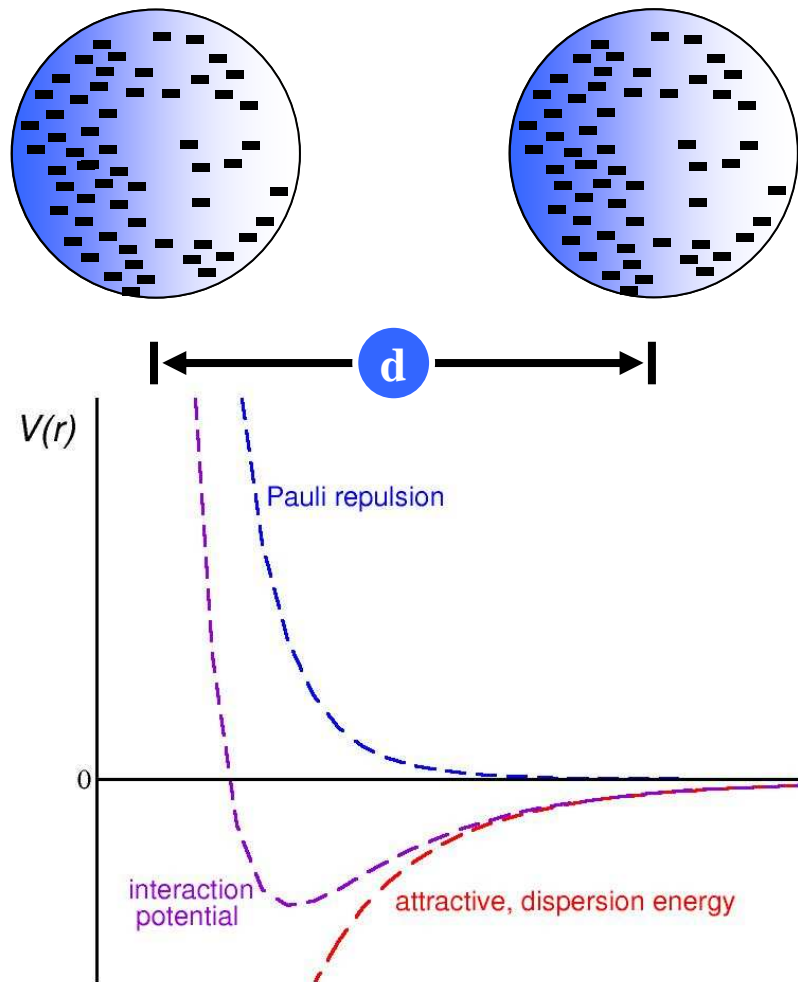
First Principles simulations of vdW complexes



- **Quantum chemical methods - MP2 and CCSD (T)**
 - Wave-function based techniques
 - Successful in describing non-local correlations
 - Basis set quality limits system size to a few atoms
 - **Density functional theory:**
 - Total energy is a functional of ρ
 - Better scaling with system size
 - Standard E_{xc} unable to account for long range van der Waals forces
-

Ideal Method: Scale like DFT, but is comparable in accuracy to QC methods

van der Waals interactions



Correlated spontaneous and induced dynamic fluctuations in electron distribution can result in net Coulomb interactions

The vdW-DF

$$E[\rho] = E_{\text{ion-ion}}[\vec{R}_i] + \overset{\text{K. E. of } e^-}{T_s[\rho]} + \underset{e^- - e^-}{E_H[\rho]} + \int \underset{e^- \text{-ion}}{V_{\text{ext}}(\vec{r})\rho(\vec{r})d^3\vec{r}} + \boxed{E_{\text{xc}}[\rho]} \overset{\text{exchange and correlation}}{}$$

Criteria for a workable vdW E_c functional:

- account for long range (vdW) correlations
- seamless return to short range form (LDA or GGA) for local interactions
- feasible and easy to implement

$$E_c[\rho] = E_c^0[\rho] + E_c^{\text{nl}}[\rho]$$

(LDA)

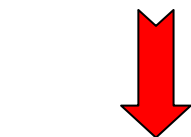
Dion, Rydberg, Schröder, Langreth and Lundqvist, Phys Rev. Lett. **92**, 246491 (2004)

The vdW-DF

$$E_C^{\text{nl}}[\rho] = \frac{1}{2} \int d^3\vec{r} \int d^3\vec{r}' \rho(\vec{r}) \Phi(\vec{r}, \vec{r}') \rho(\vec{r}')$$

No adjustable parameters!

Vanishing in uniform electron gas limit ensures no double counting with LDA



$$\Phi(\delta, D)$$

$$\delta = \frac{1}{2} \frac{(q - q')}{(q + q')}$$

$$D = \frac{(q + q')}{2} |r - r'|$$

where $q = q(\rho(\vec{r}), \nabla\rho(\vec{r}))$

True non-local density functional!

$$E_{xc}[\rho] = E_X^0[\rho] + E_C^0[\rho] + E_C^{\text{nl}}[\rho]$$

(revPBE) (LDA)

Greatly reduces computational demand as kernel can be pre-tabulated!

Dion, Rydberg, Schröder, Langreth and Lundqvist, Phys Rev. Lett. **92**, 246491 (2004)

vdW-DF Procedure

1. **Self-consistent GGA (revPBE) calculations**
 - 50 Ry cutoff
 - Norm-conserving Pseudopotentials
 - Abinit, Dacapo, PARSEC (real space DFT), Siesta
 2. To incorporate vdW interactions we use $\rho(r)$ from GGA calculations to compute E_c^{nl}
- ∇ **Self-consistent version available – gives same results as post-processing method.**

Dion, Rydberg, Schröder, Langreth and Lundqvist, Phys Rev. Lett. **92**, 246491 (2004)
Thonhauser, Cooper, Li, Puzder, Hyldgaard and Langreth, PRB, **76**, 125112, (2007)

vdW-DF and petascale computing

System	# e ⁻ (atoms)	# grid pts.	revPBE	vdW-DF*
Base pair	98 (30)	45431	73 min	40 min
Base pair step	196 (60)	89044	350 min	175 mins

*vdW-DF post-processing method (self consistent vdW-DF 3-6 x revPBE)

***AMD Opteron 2.20 Ghz, 4GB Mem, 1 MB cache**

A typical gene ~ 100 - 200 base pairs (3000 – 6000 atoms)

Proteins ~ 2000 - 4000 atoms

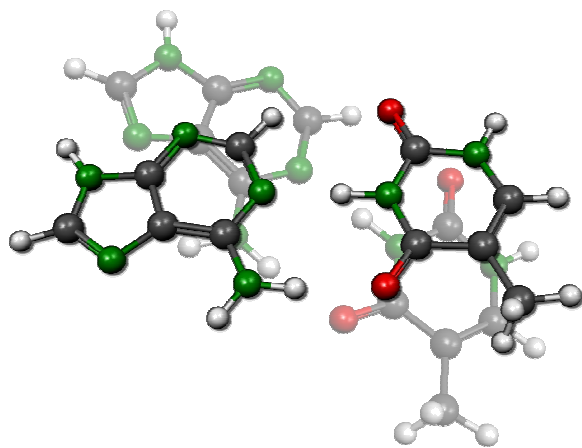
†without inclusion of solvent molecules

vdW-DF advantages for petascale computing:

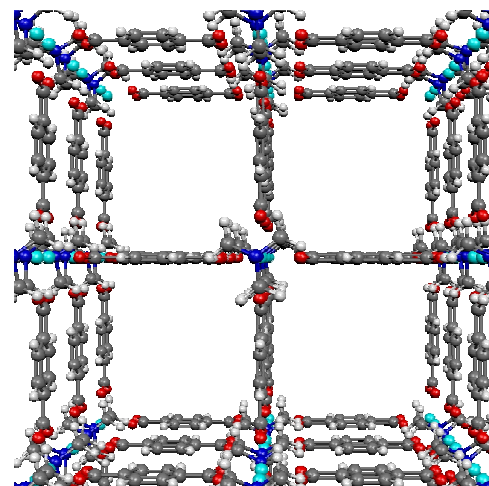
- easily parallelizable
- infrequent communication for larger systems
- better than $\mathcal{O}(N^3)$ scaling
 - system size limited by rest of DFT calculation
 - great for use with linear scaling DFT methods

Applications of the van der Waals Density Functional

Stacking interactions and the Twist of DNA



Hydrogen Storage in MOF materials

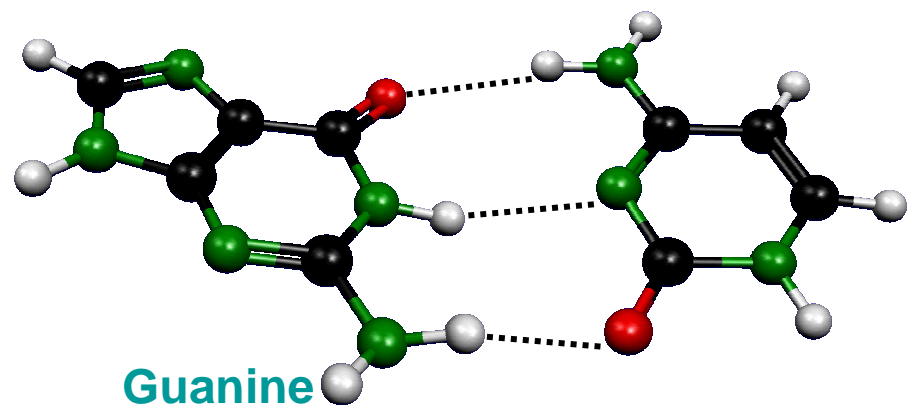
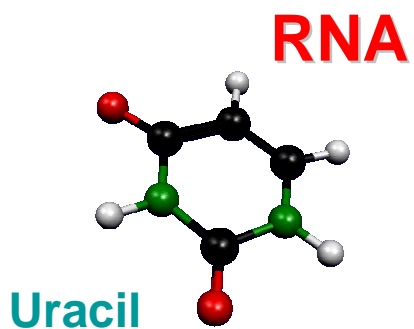


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RUTGERS
THE STATE UNIVERSITY
OF NEW JERSEY

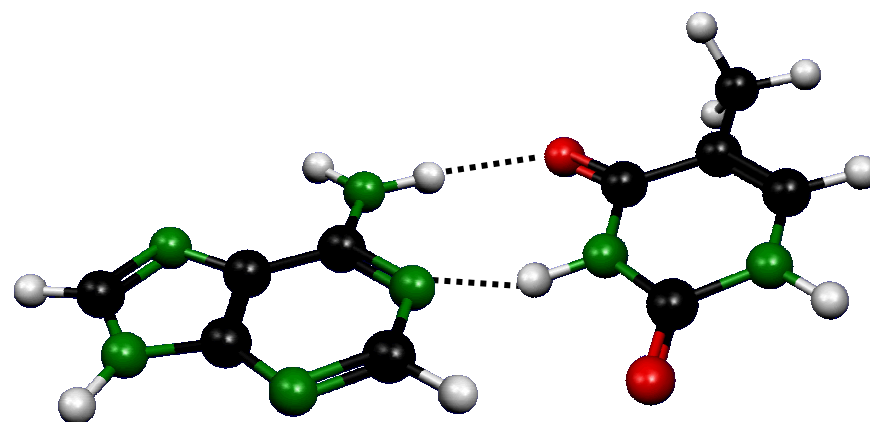
Stacking interactions and the Twist of DNA

A brief description of DNA



Guanine

Cytosine



Adenine

Thymine

Motivation



Research has shown:

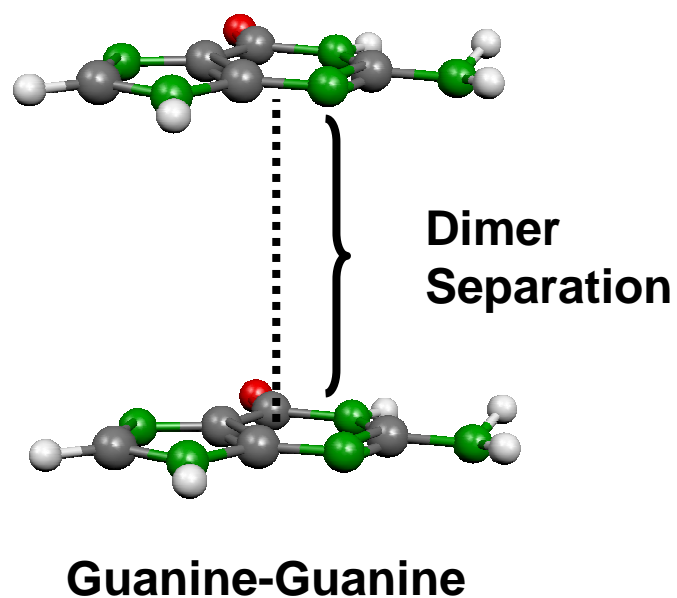
- Transcription and replication
- Interaction of DNA with proteins and viruses
- Intercalation of chemotherapy drugs alter the structure of DNA

-
- Drug development
 - Gene therapy
 - Understanding mutations
 - Genetic disorders

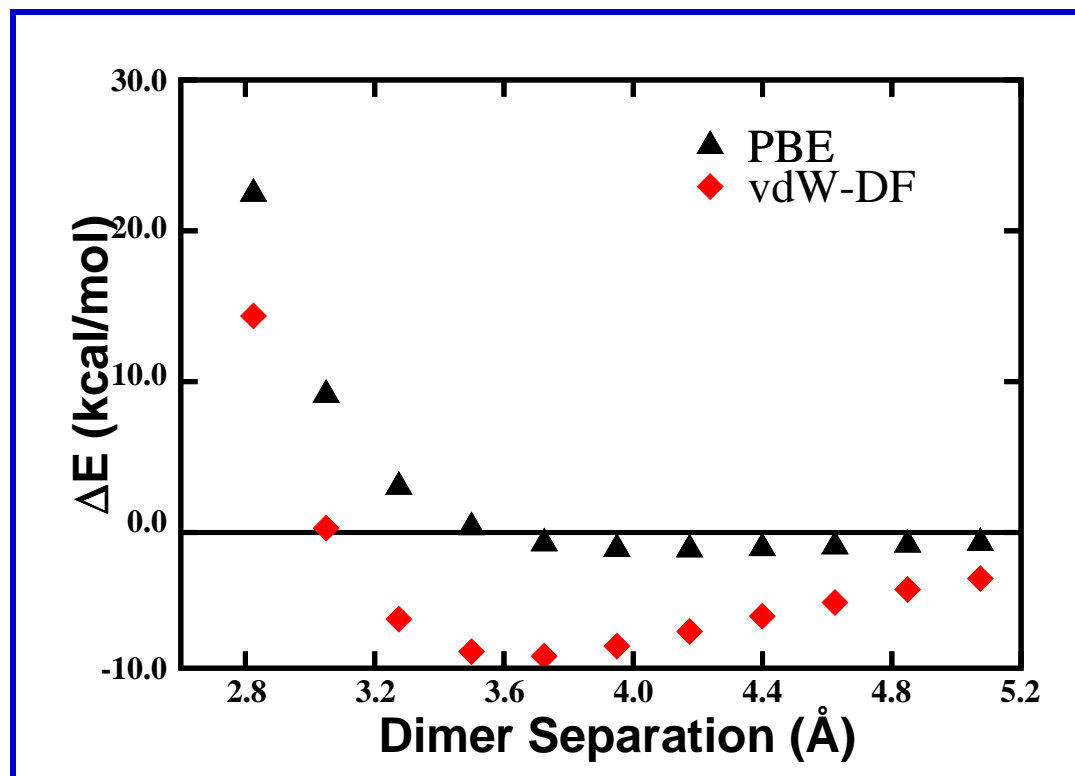
To develop a theoretical understanding of the influence of base pair stacking interactions on the structure of DNA

Are vdW interactions necessary?

Consider a stack of two nucleic acids – similar to single stranded DNA/RNA!

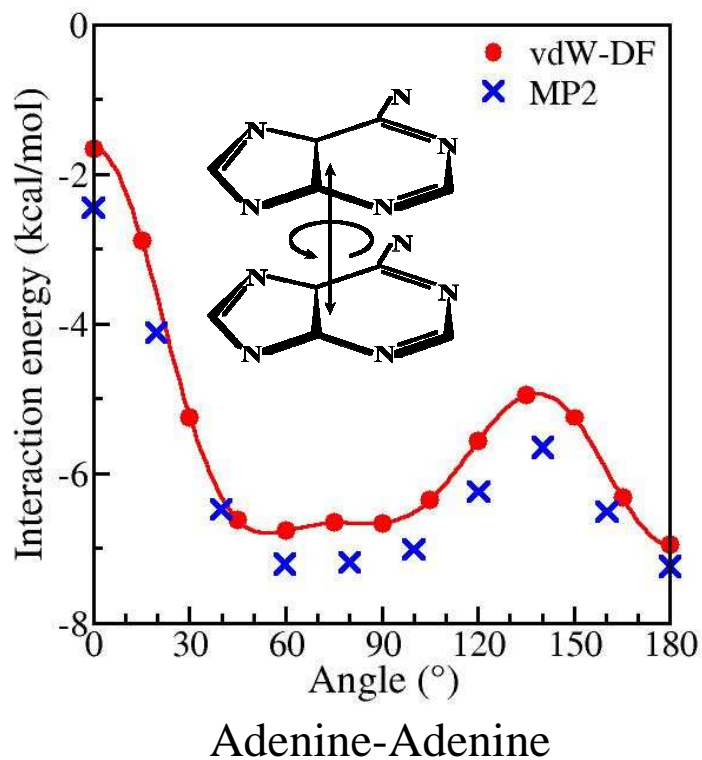


$$\Delta E_{\text{MP2}} = \sim -10 \text{ kcal/mol}$$



Elstner et al. J. Chem. Phys. 114, 5149 (2001)

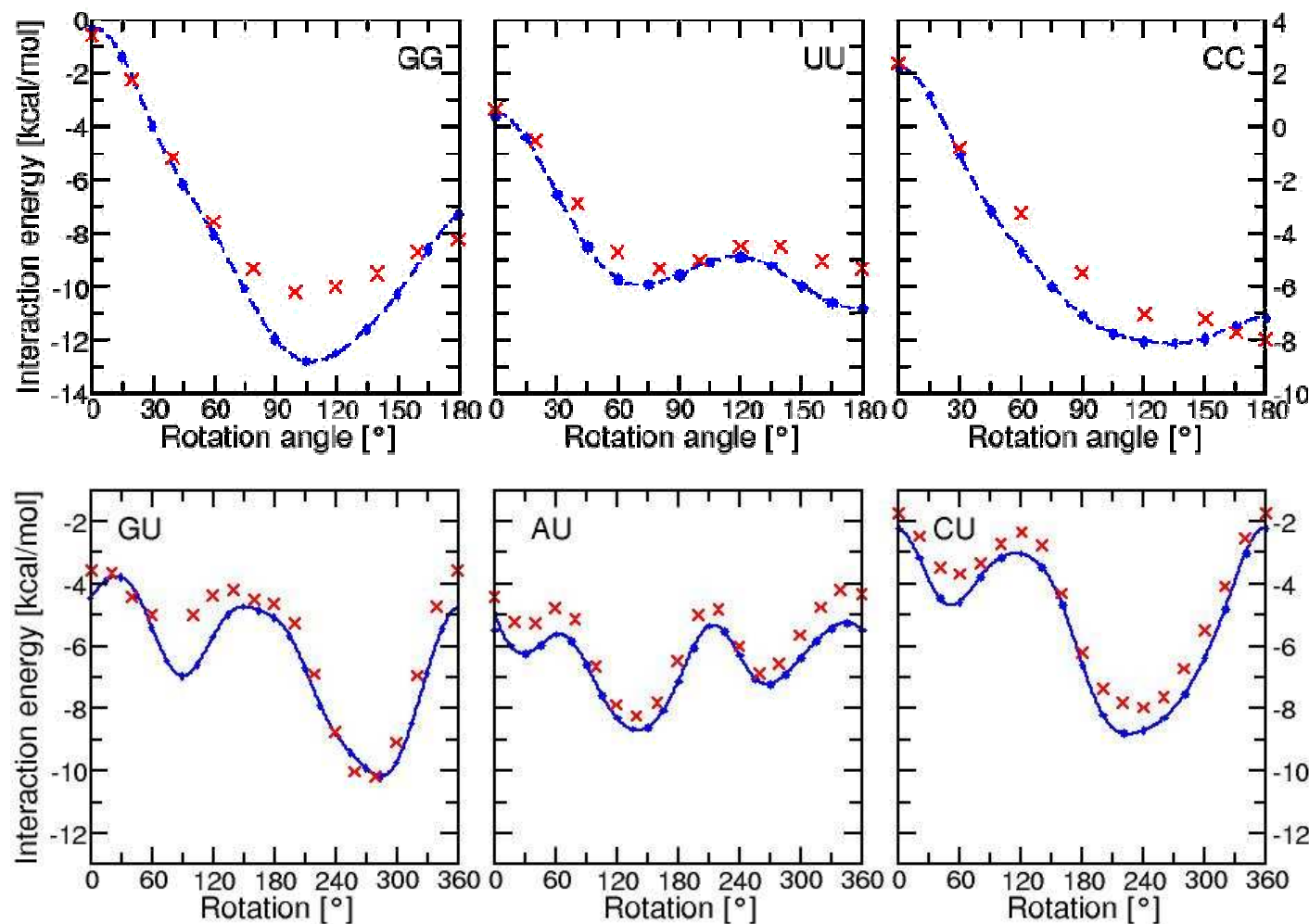
Stacking interactions of nucleic acids



MP2 calculations by: Elstner et al. J. Chem. Phys. **114**, 5149 (2001)

Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, JACS, **130**, 1304, (2008)

ΔE vs. rotation angle



vdW-DF @ 3.40 Å

MP2 @ 3.40 Å

Elstner et al. J. Chem. Phys. **114**, 5149 (2001)

Cooper, Thonhauser and Langreth JCP, **128**, 204102 (2008)

S22 data set

(ΔE in kcal/mol)	vdW-DF	QC	BLYP-D (04)	BLYP-D (07)
AT (WC)	-15.20	-16.37	-15.01	-17.19
Benzene-CH ₄ (C ₃)	-1.57	-1.50	-0.90	-1.37
Benzene-H ₂ O (C _s)	-2.72	-3.28		-4.16
Benzene dimer (C _{2v})	-2.28	-2.74	-2.03	-2.76
Benzene dimer (C _{2h})	-2.80	-2.73	-2.00	-2.35
AT (stack)	-9.55*	-12.23	-10.47	-12.85

*Not optimized

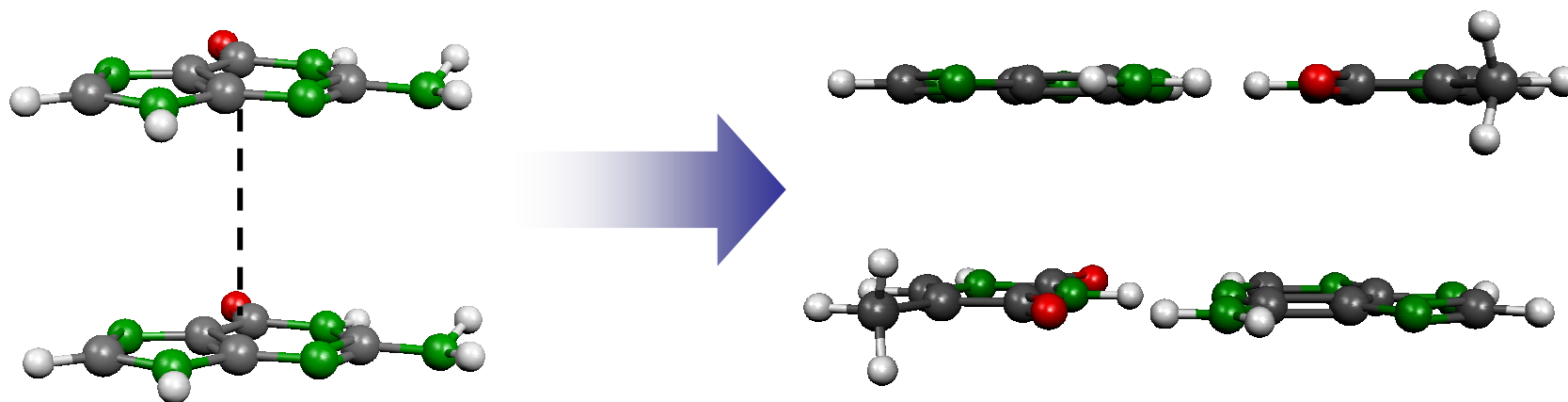
vdW-DF: Compiled in V. R. Cooper, T. Thonhauser, D. Langreth, J. Chem. Phys. (in press).

QC: P. Jurecka, J. Sponer, P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).

BLYP-D (04): S. Grimme, J. Comp. Chem. **25**, 1463 (2004).

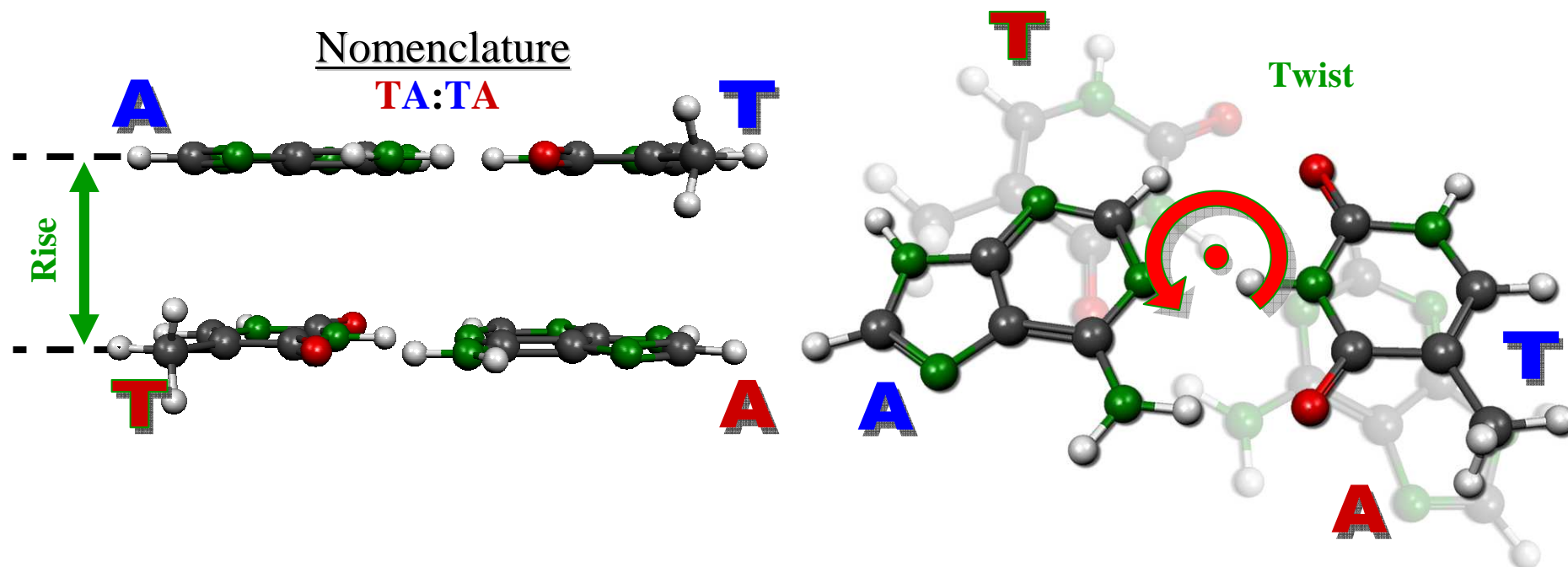
BLYP-D (07): S. Grimme, et al. Org. Biomol. Chem. **5**, 741 (2007).

Stacking interactions of nucleic acids



vdW-DF is *comparable* in accuracy to MP2,
and can be easily applied to larger systems
e.g. stacked nucleic acid base pairs

Watson-Crick base pair stacking



From the Nucleic Acid Database[†]: [<http://ndbserver.rutgers.edu>]

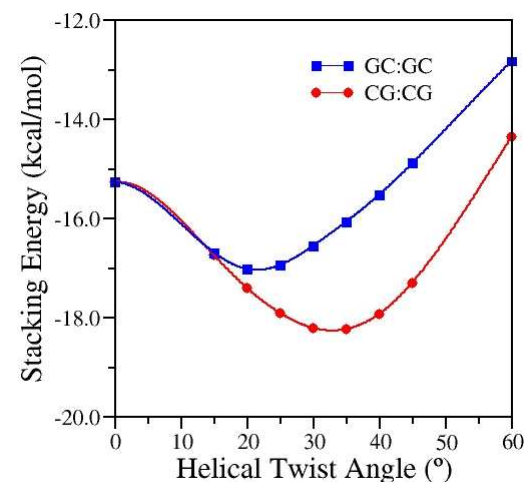
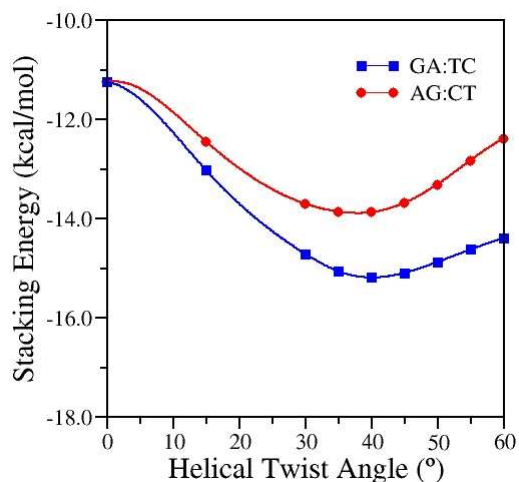
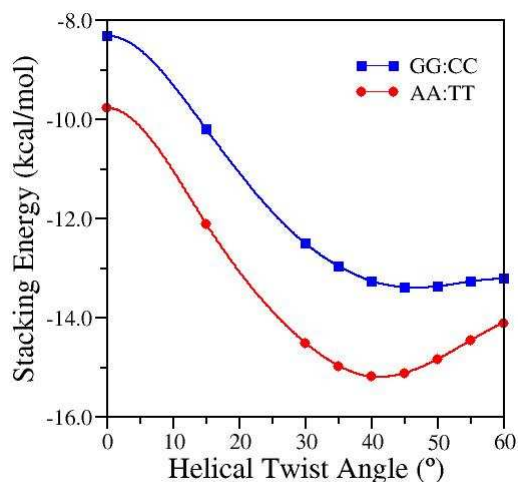
$$\text{Twist} = 36.0 \pm 6.8^\circ$$

$$\text{Rise} = 3.32 \pm 0.19 \text{ \AA}$$

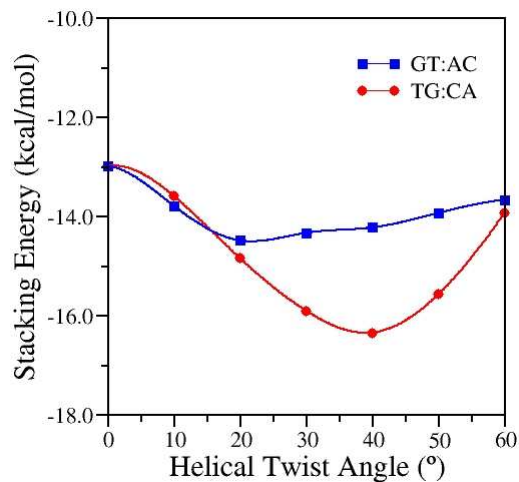
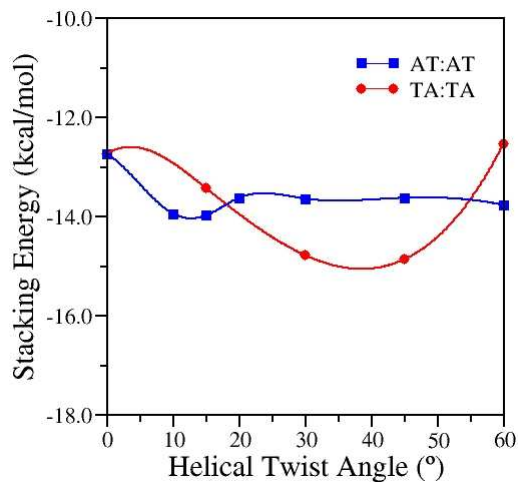
Data for crystalline B-DNA

**No sugar phosphate backbone,
or solvent molecules!**

Watson-Crick base pair stacking



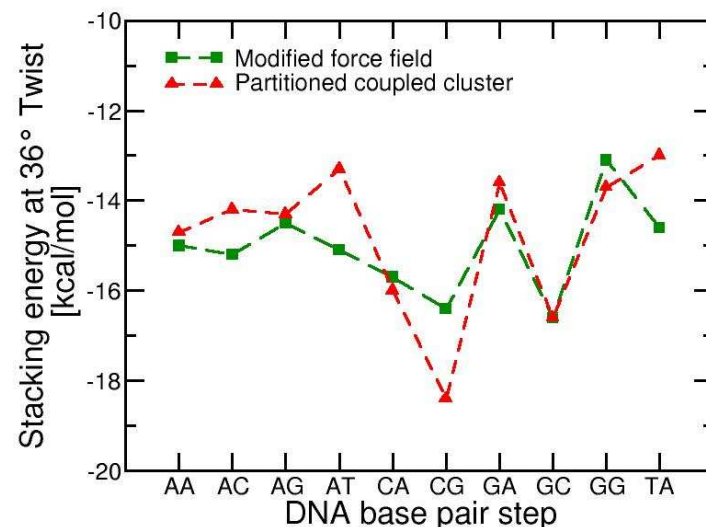
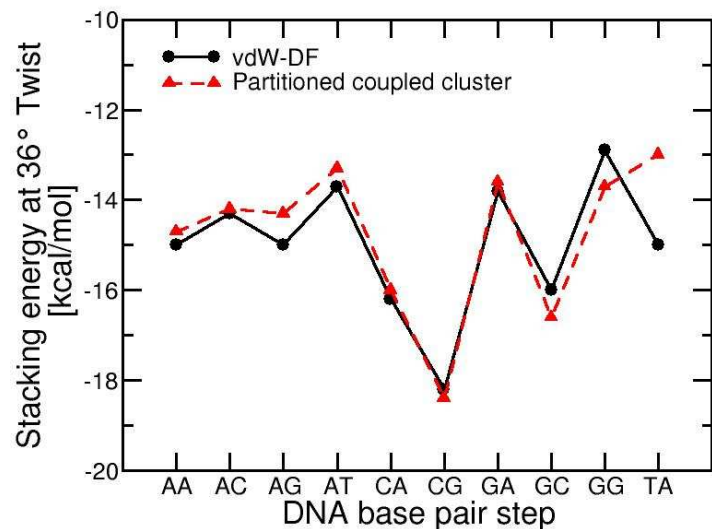
Stacking interactions important for defining DNA structural parameters



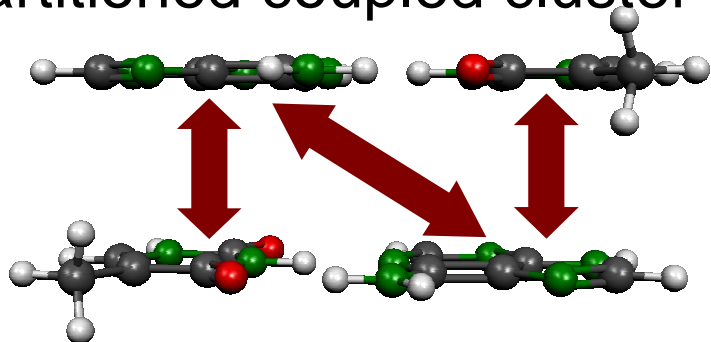
Our results	Nucleic acid database
$33.7^\circ \pm 9.4^\circ$	$36.0^\circ \pm 6.8^\circ$
$3.52 \pm 0.05 \text{ \AA}$	$3.32 \pm 0.19 \text{ \AA}$

Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, JACS, **130**, 1304, (2008)

Comparison with QC Methods



Comparison of vdW-DF* with partitioned coupled cluster**

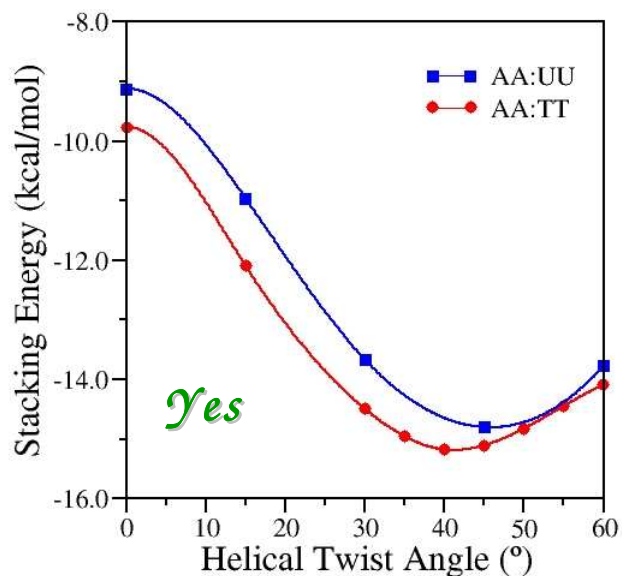


Comparison of Amber force field (modified** for better fit) with partitioned coupled cluster.

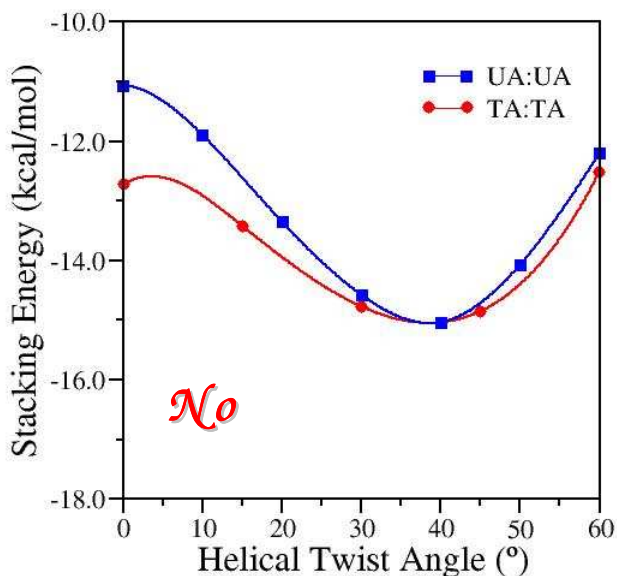
Šponer, J. et al. *Chem. Eur. J.* **2006, *12*, 2854

*Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, *JACS*, **130**, 1304, (2008)

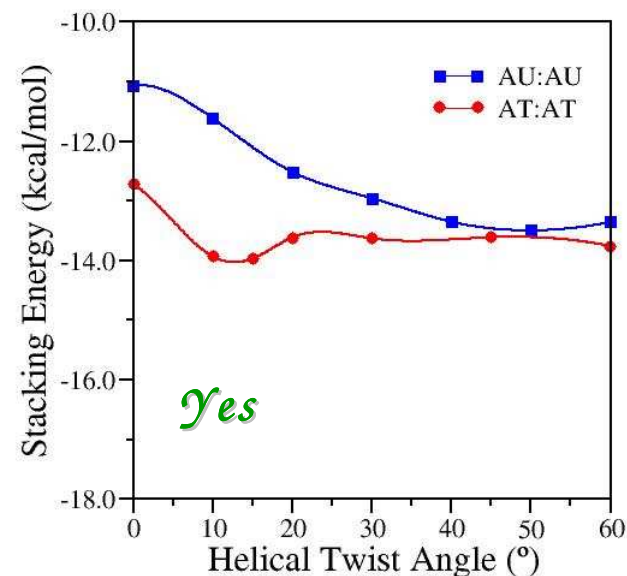
Thymine Interactions in DNA



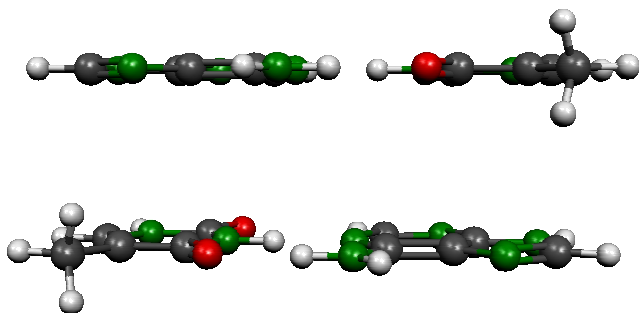
$$\Delta E_{@ 36^\circ} = 329 \text{ cal/mol/b.p.}$$



$$\Delta E_{@ 36^\circ} = 10 \text{ cal/mol/b.p.}$$



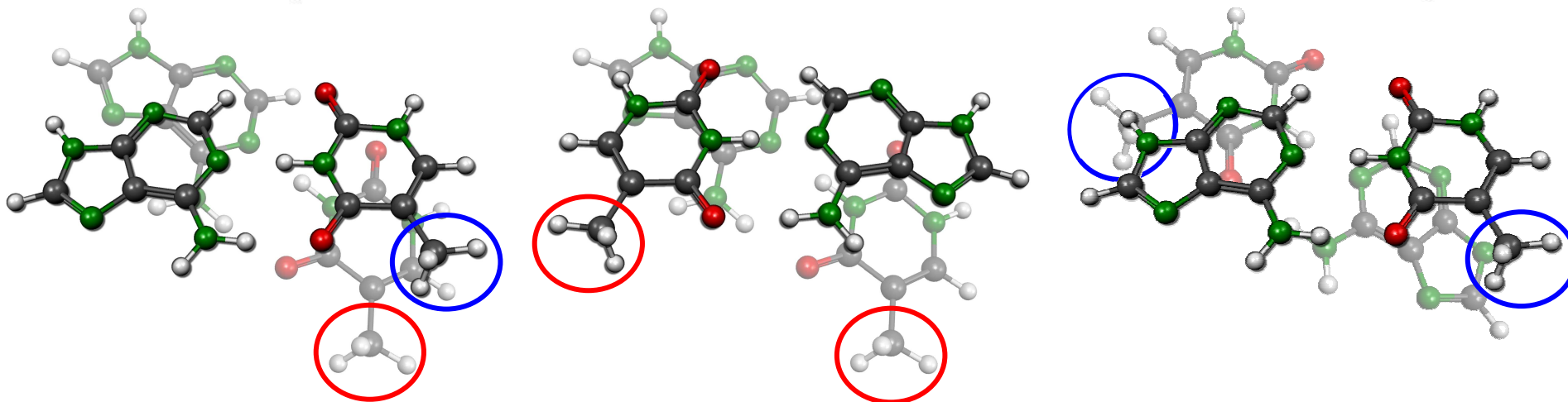
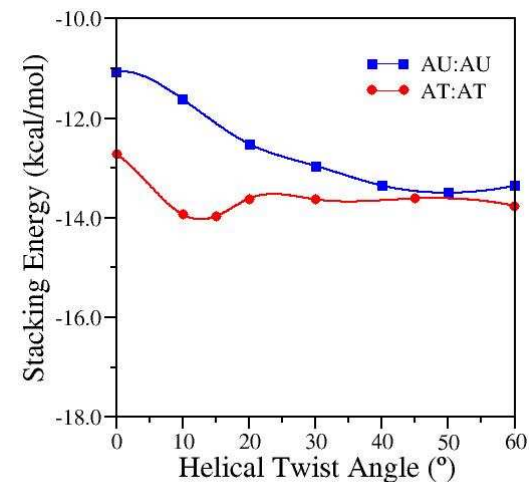
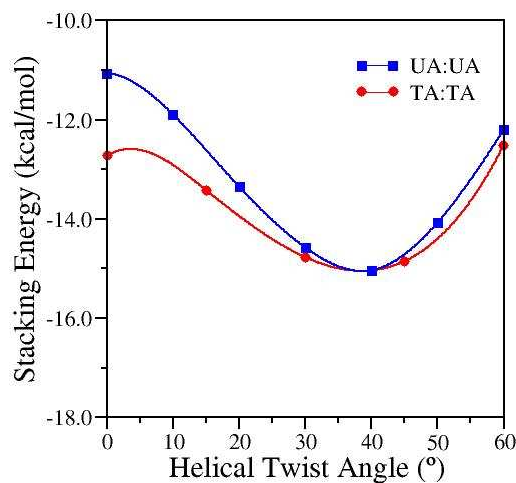
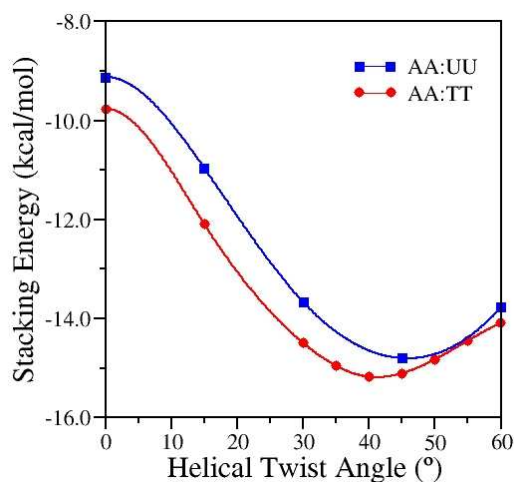
$$\Delta E_{@ 36^\circ} = 231 \text{ cal/mol/b.p.}$$



Stacked
nucleic acid
base pairs

Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, JACS, **130**, 1304, (2008)

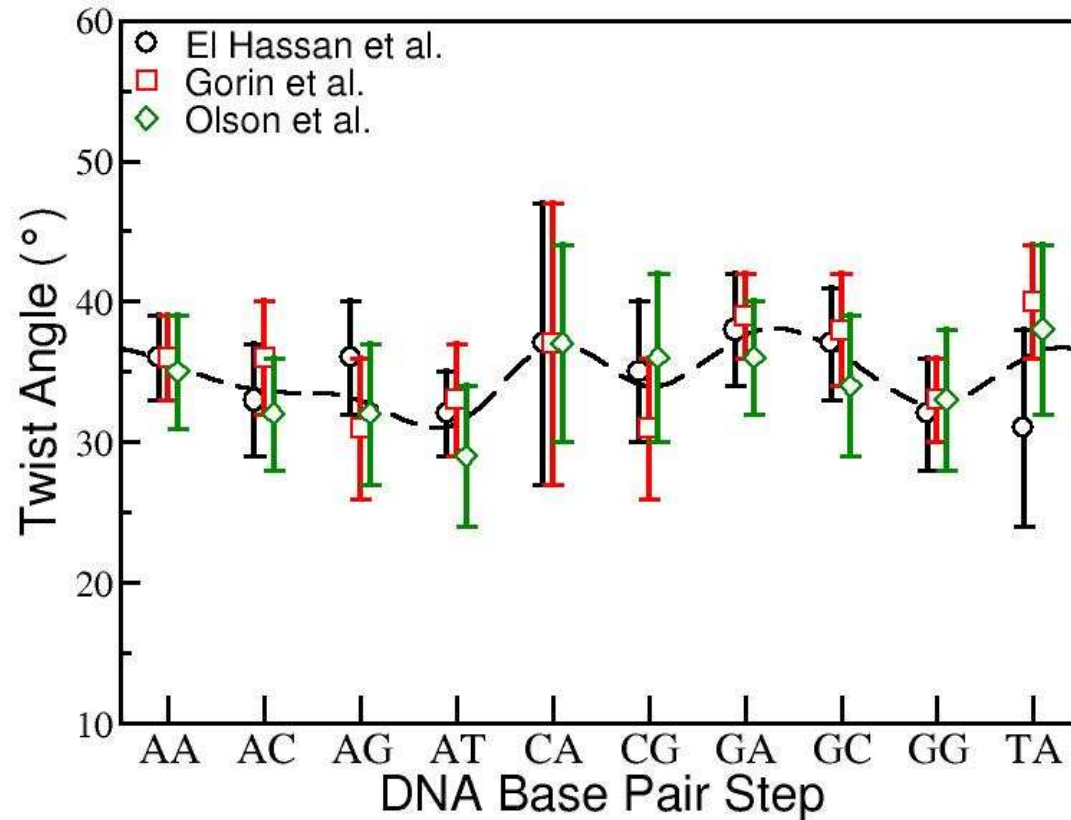
The Methyl Effect



Methyl-nucleic acid/methyl-methyl interactions contribute to thymine stabilization

Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, JACS, **130**, 1304, (2008)

Sequence-dependent Twist

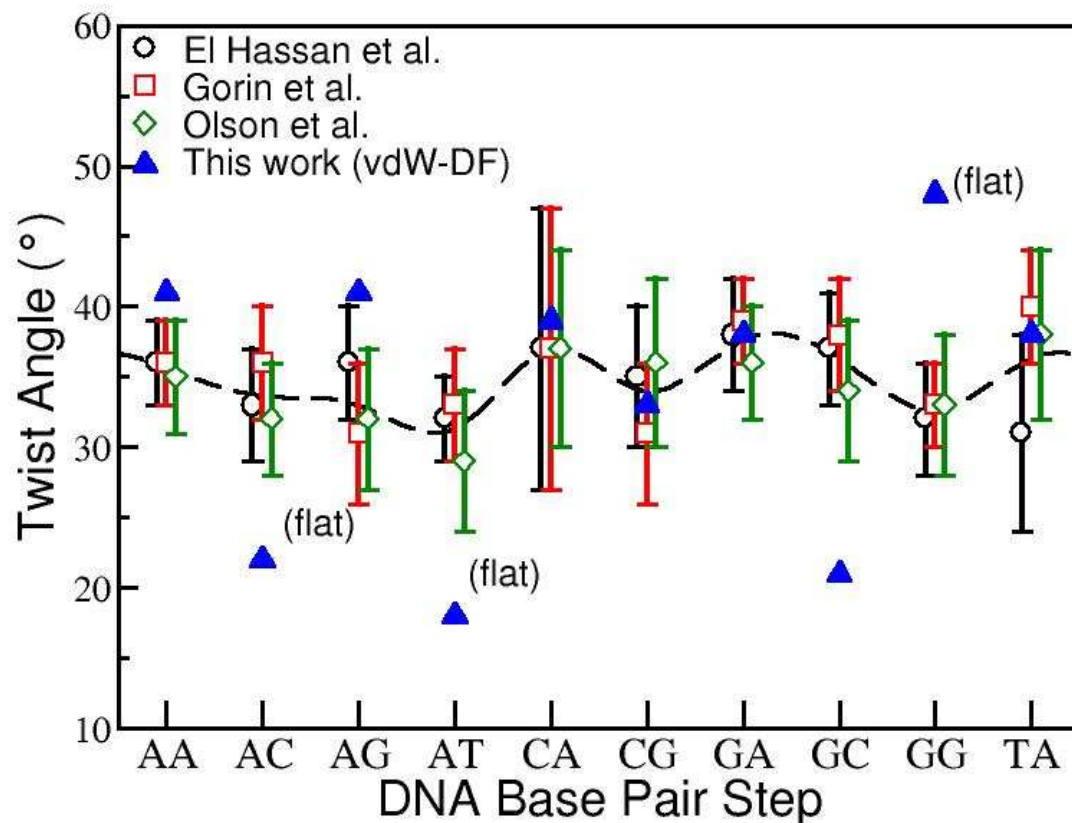


El Hassan, M. A.; Calladine, C. R. *Phil. Trans.: Ser. A* **1997**, 355, 43.

Gorin, A. A.; Zhurkin, V. B.; Olson, W. K. *J. Mol. Biol.* **1995**, 247, 34.

Olson, W. K.; Gorin, A. A.; Lu, X.-J.; Hock, L. M.; Zhurkin, V. B. *PNAS* **1998**, 95, 11163

Sequence-dependent Twist



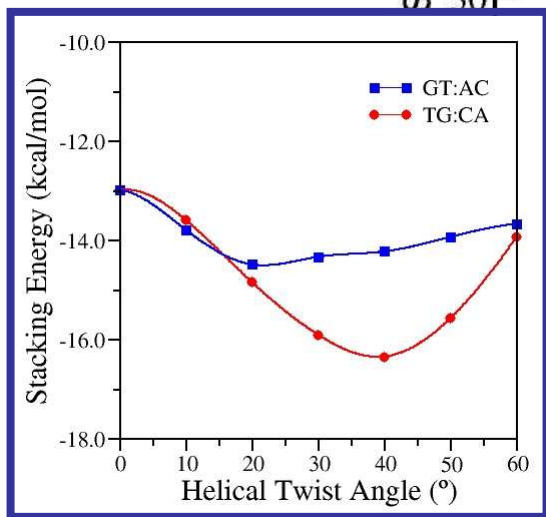
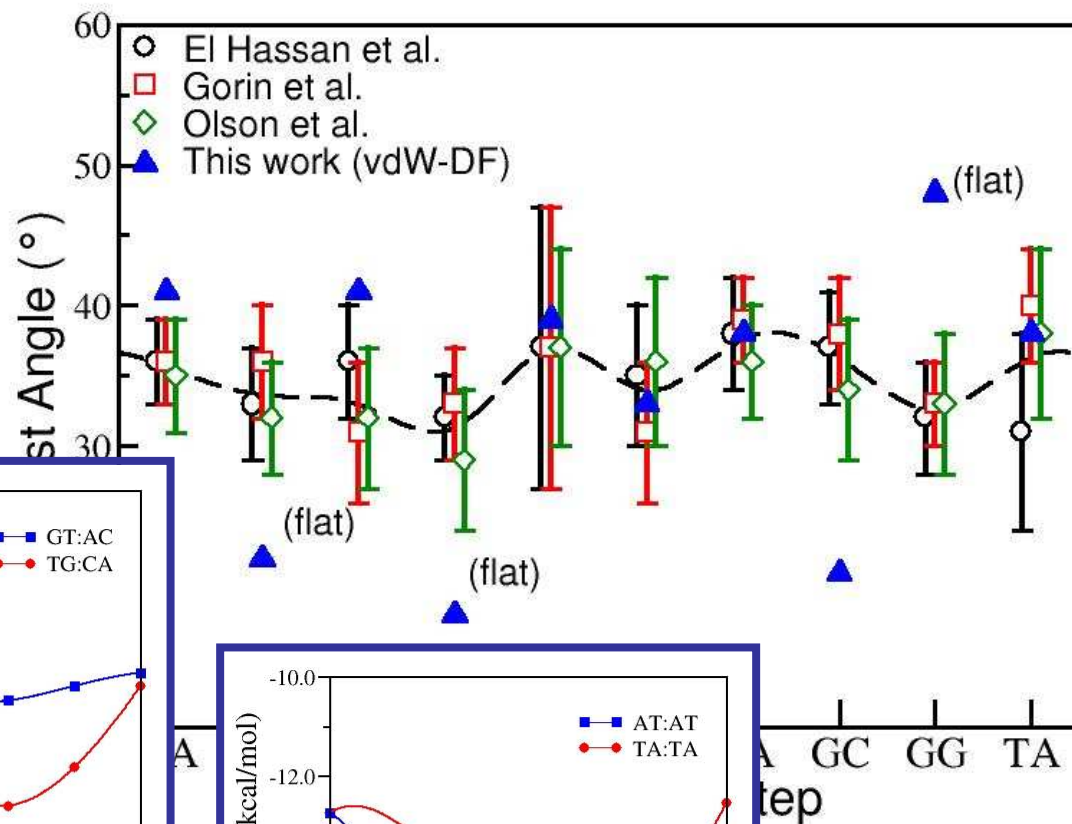
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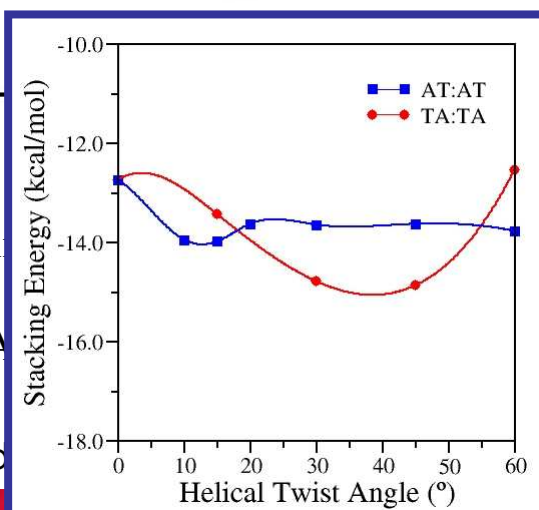
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Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, *JACS*, **130**, 1304, (2008)

Sequence-dependent Twist



Olson, W. K.; Gorin, A. A.



A GC GG TA
step

97, 355, 43.

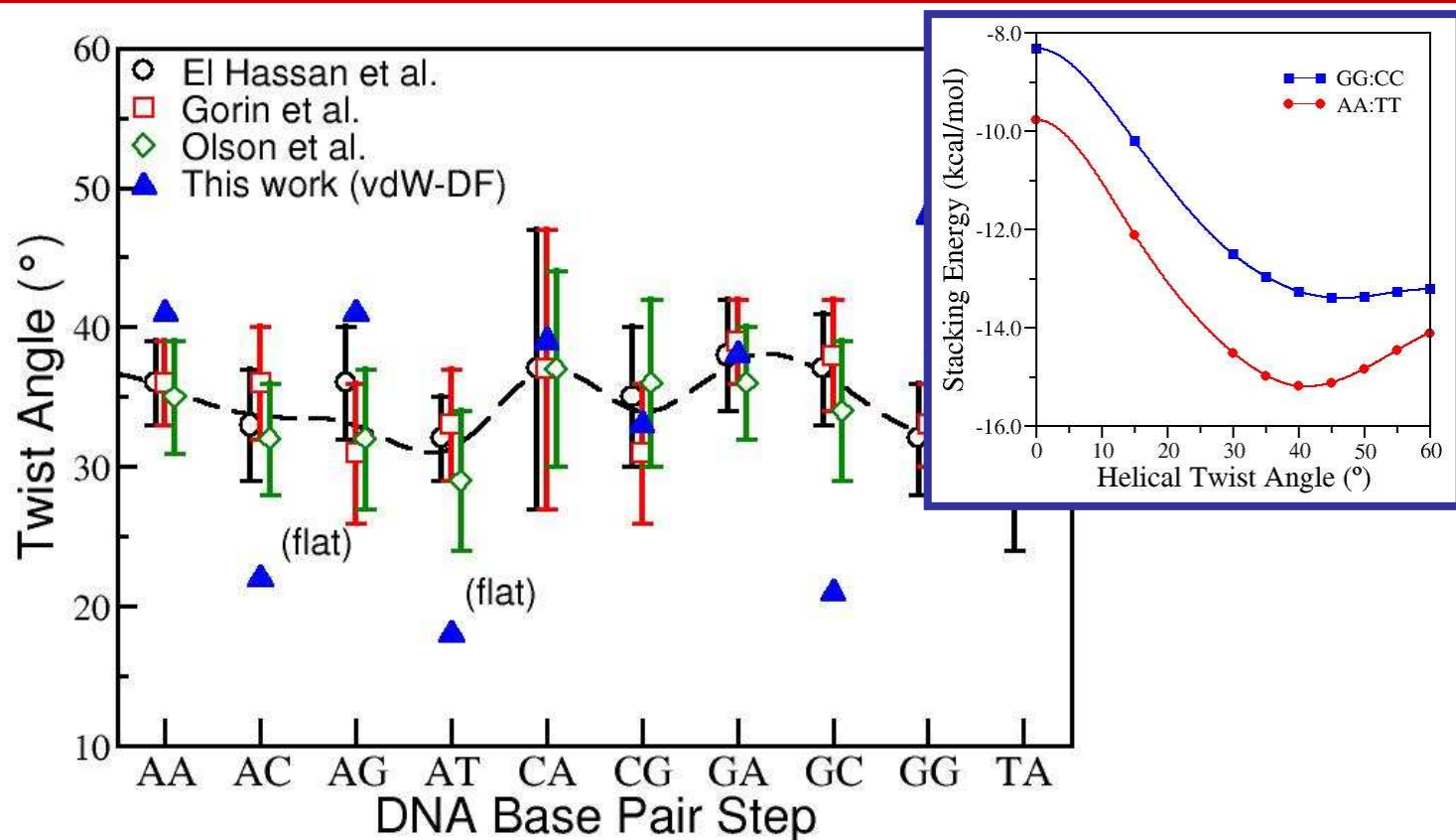
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S, 130, 1304, (2008)

Cooper, Thonhauser, Puzder, Schröder

Sequence-dependent Twist



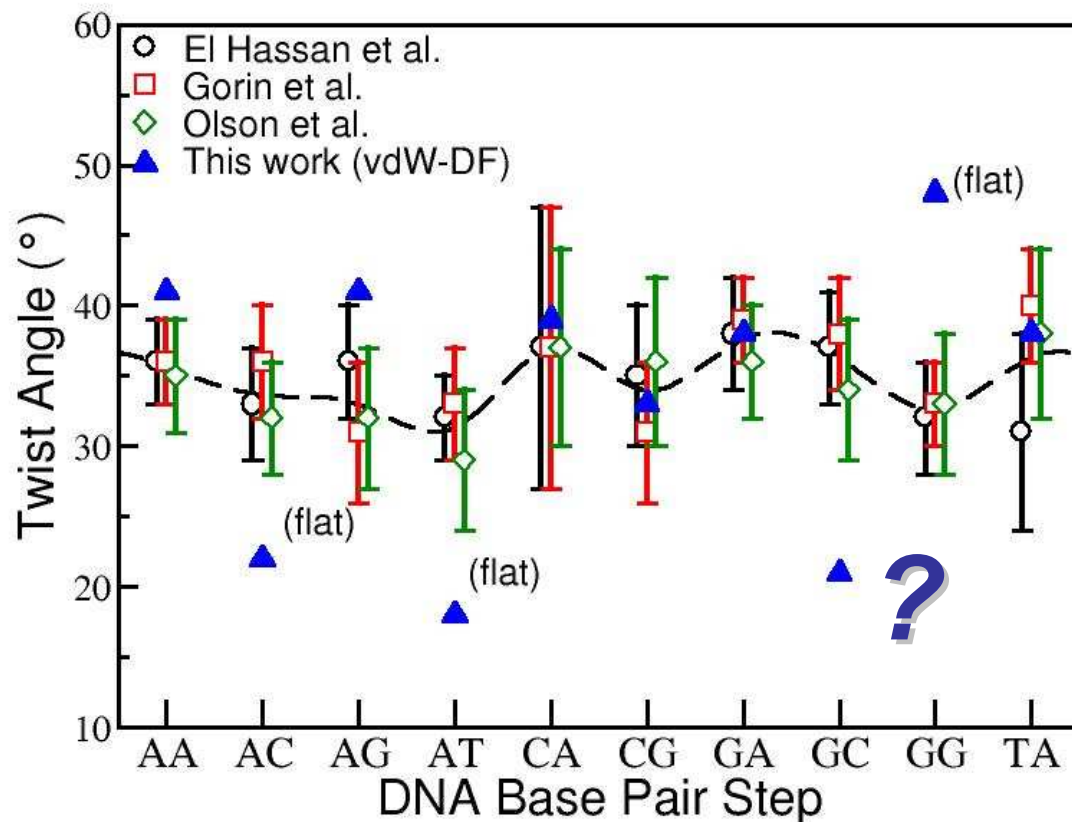
El Hassan, M. A.; Calladine, C. R. *Phil. Trans.: Ser. A* **1997**, 355, 43.

Gorin, A. A.; Zhurkin, V. B.; Olson, W. K. *J. Mol. Biol.* **1995**, 247, 34.

Olson, W. K.; Gorin, A. A.; Lu, X.-J.; Hock, L. M.; Zhurkin, V. B. *PNAS* **1998**, 95, 11163

Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, *JACS*, **130**, 1304, (2008)

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Olson, W. K.; Gorin, A. A.; Lu, X.-J.; Hock, L. M.; Zhurkin, V. B. *PNAS* **1998**, 95, 11163

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Metal-organic framework materials

H₂ storage

- Any practical methods of storage should:
 - high gravimetric densities
 - safe, fast and reversible @ ambient T°,p (atm)
 - cost effective
- Present DOE mandate: 9 wt. % by 2015 (including the entire storage device!)
- Current devices store H₂ as either compressed gas or a liquid – extremely unsafe, and inefficient



Honda FCX Clarity

Solid state storage materials are the way to go!

Metal Hydrides

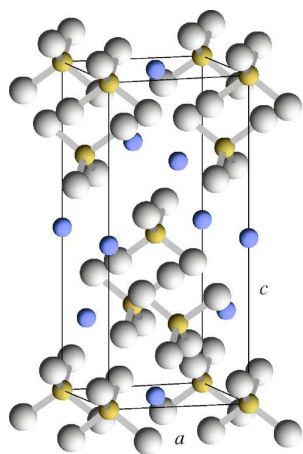
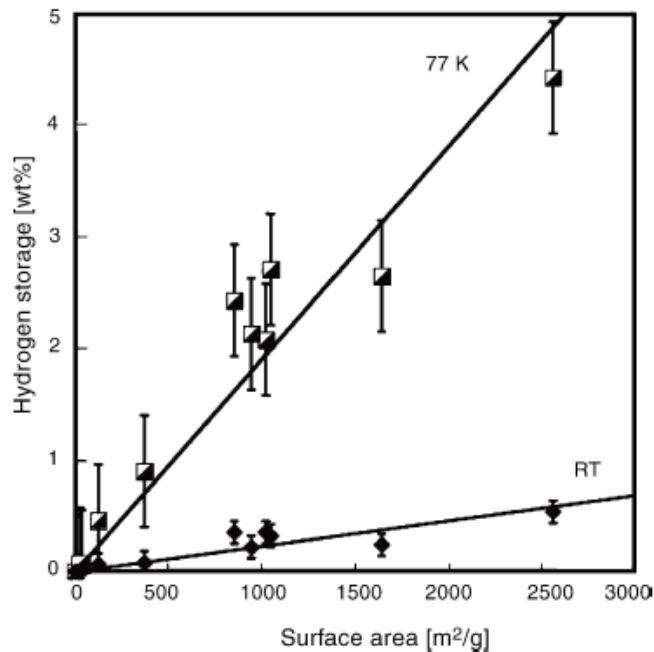


Figure taken from
Peles and Chou, PRB
73, 184302 (2006)

- Store H_2 as dissociated H atoms in a metal lattice
- Advantage
 - relatively high gravimetric densities at ambient T° and moderate p
- Disadvantages
 - poor reversibility
 - slow adsorption and desorption rates
- Doping (e.g. with Ti) can enhance kinetics

Carbon based H₂ storage



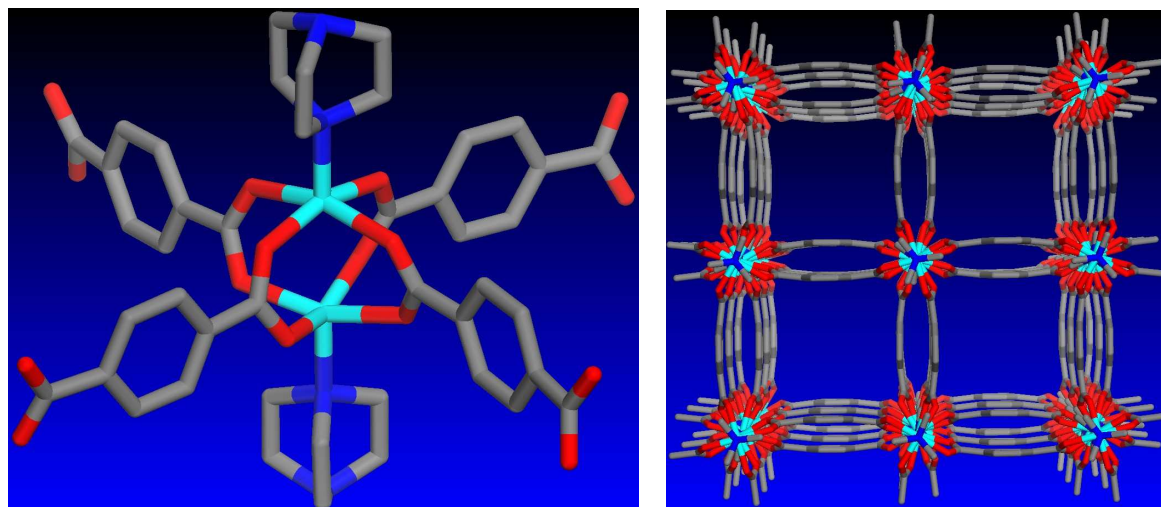
Hirscher et al. J. Alloys Compd. **404-406**, 399, (2005)

- H₂ stored as physisorbed molecules
 - Graphite, buckyballs, carbon nanotubes
- Advantages
 - Excellent reversible H₂ storage,
 - Storage density directly linked to available surface area
- Disadvantages
 - High cost
 - Low storage capacity
 - Poor sample reproducibility

Metal-organic framework materials

Metal-organic framework (MOF) materials consist of metal ions or clusters linked through molecular bridges

- Large surface area in pores and
 - Possible H₂/metal interactions
 - Low cost, high yield and highly reproducible synthesis
- may make them good candidates for hydrogen storage materials

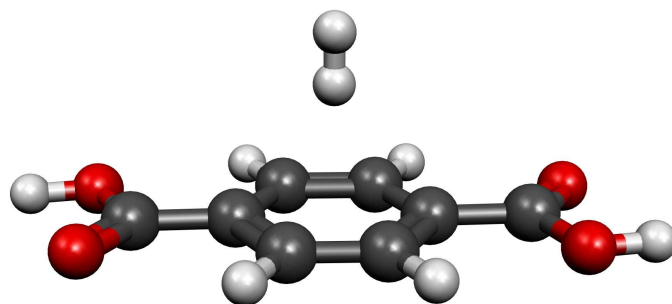


A generic MOF [M₂(bdc)₂(ted)]

[M = Co, Cu, Zn, bdc = benzene dicarboxylate, ted = tri-ethyl diamine]

Left: Sideview of column, Right: 3D framework.

First-principles simulations of MOFs



Calculations of fragments such as benzene dicarboxylate (right) are commonly used to simulate the interactions of hydrogen with MOFs.

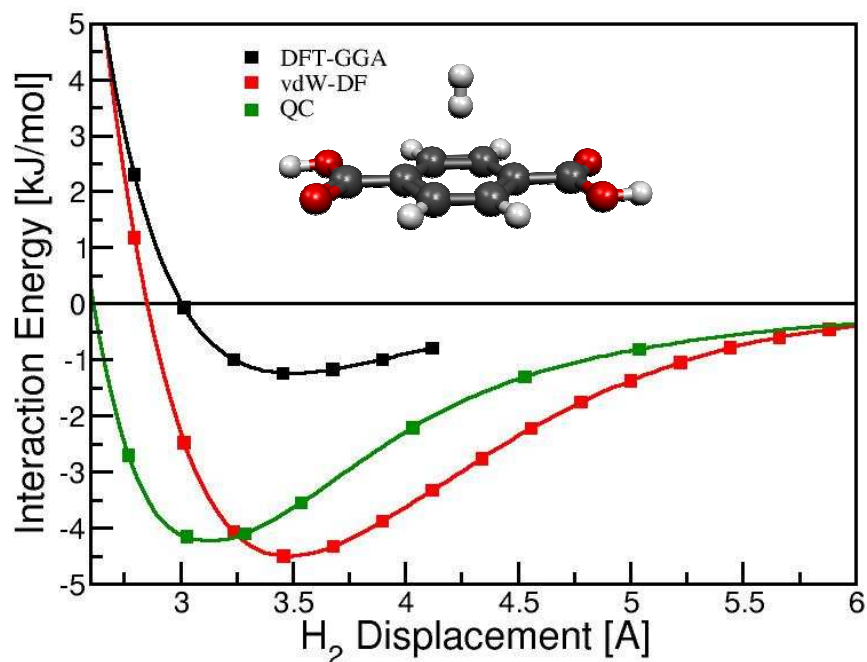
Sagara et al. J. Chem. Phys. **123**, 214707, (2005)

Outline

Goal: To use theoretical methods to explore the adsorption of H₂ within MOF materials.

- Examine differences of modeling MOF fragment and entire MOF
- Explore the importance of the metal cation

H₂ interactions with linker fragment

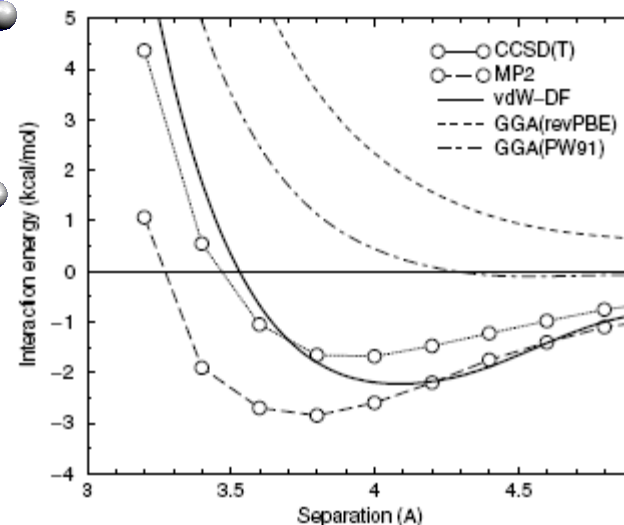
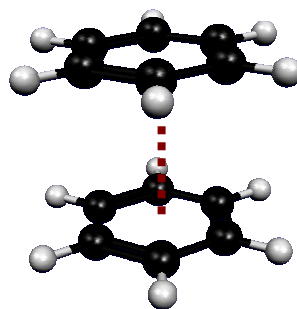
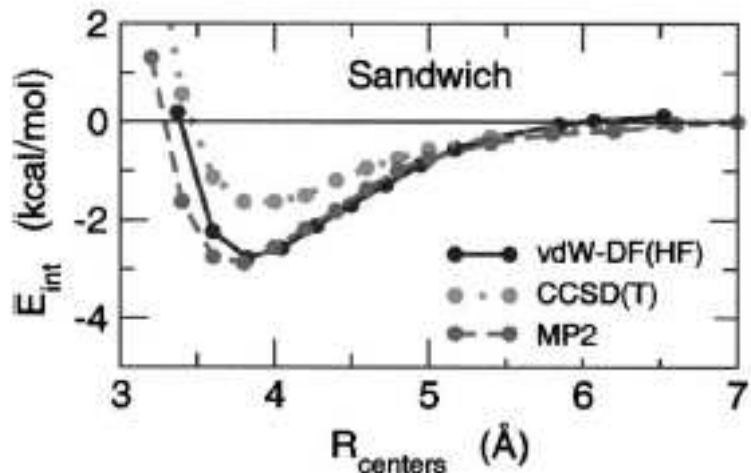


- GGA greatly underestimates binding energy
- vdW-DF agrees well with QC method.

QC calculations by: Sagara, Ortony, and Ganz J. Chem. Phys **123**, 214707 (2005)

Exchange Effects

Benzene Dimer

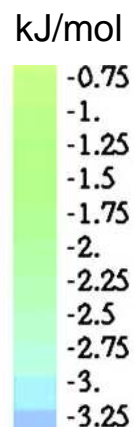
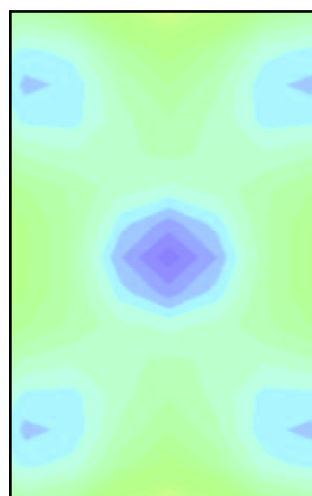


0.25-0.35 Å larger separation distances due to too repulsive exchange term.

Dion, Rydberg, Schröder, Langreth and Lundqvist, Phys Rev. Lett. **92**, 246491 (2004)

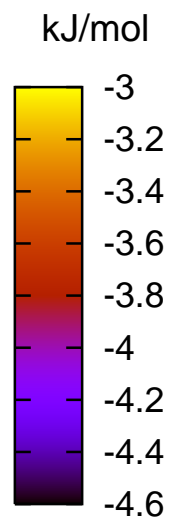
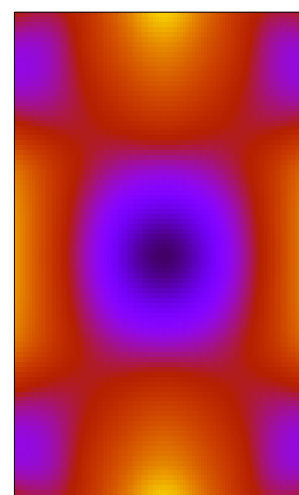
Linker potential energy surface

QC PES



fixed separation distance

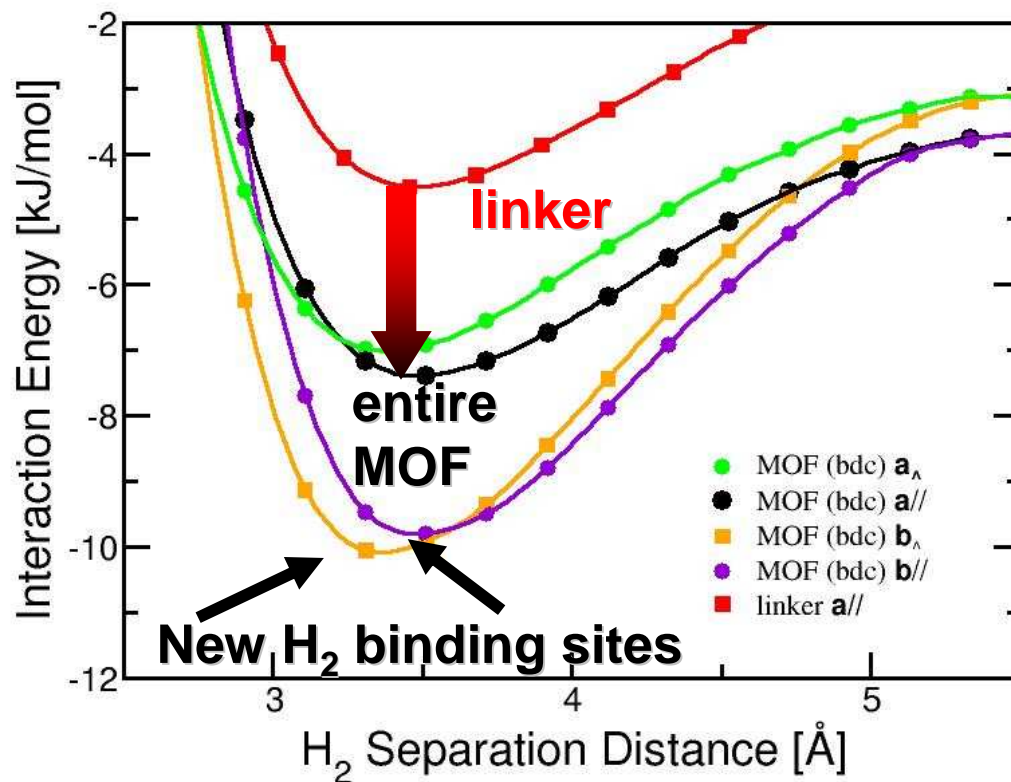
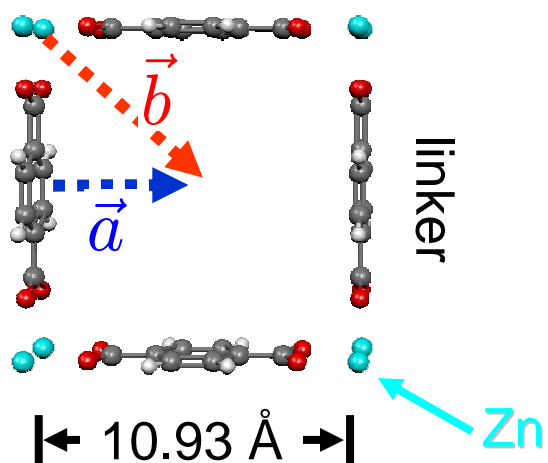
vdW-DF PES



optimized separation distance

QC calculations by: Sagara, Ortony, and Ganz J. Chem. Phys **123**, 214707 (2005)

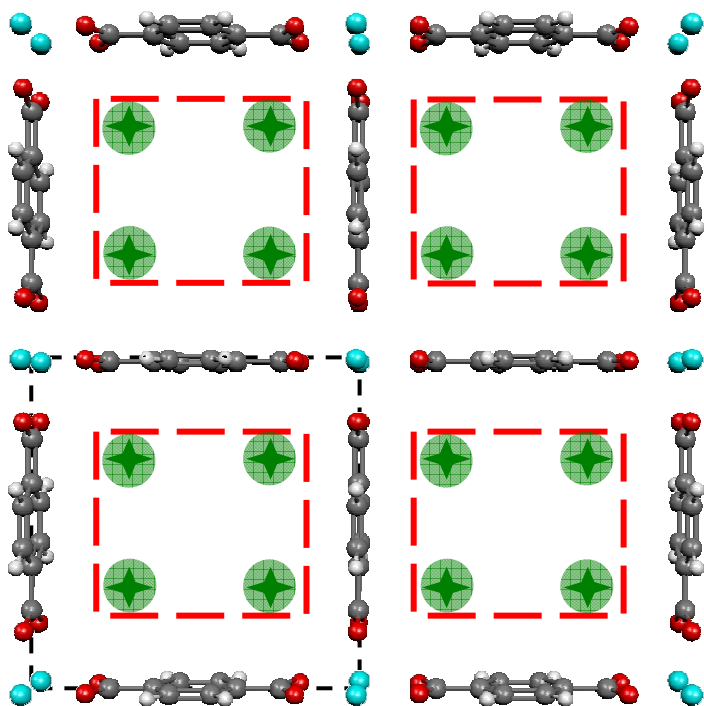
Modeling the true MOF (bdc linker)



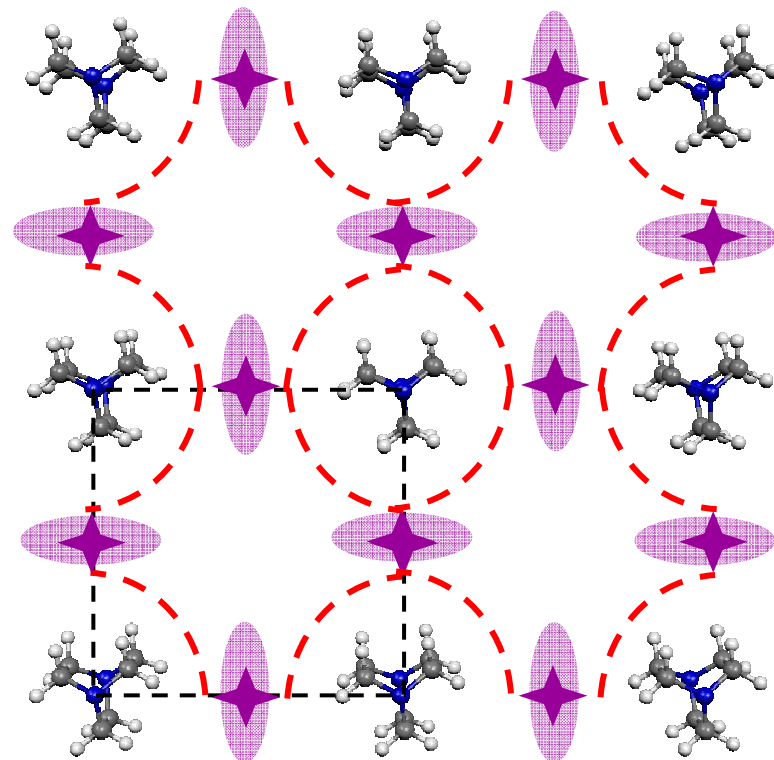
Advantages of modeling entire MOF:

- Significant difference (~3 kJ/mol) in H₂ binding E relative to fragment,
- New more stable H₂ binding sites now accessible!

Predicting H₂ adsorption sites

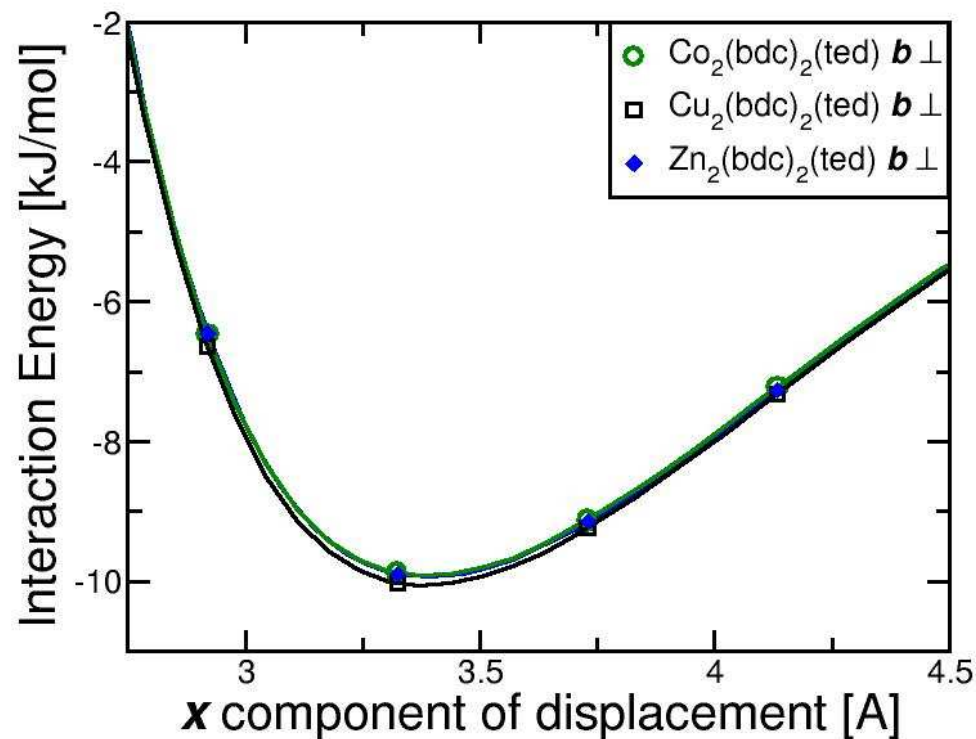


★ Linker plane preferred binding site,
 $\Delta E = -10.0$ kJ/mol



★ Pillar plane preferred binding site,
 $\Delta E = -11.1$ kJ/mol

Metal Cation Substitution



Results suggest that there is a negligible difference upon substitution!

Conclusion

- Good agreement observed between high level QC method and vdW-DF
- Demonstrated the importance of vdW forces for defining DNA Twist and Rise
- Showed how stacking interactions can account for the stabilization of DNA over RNA
- Highlight the importance of studying the entire MOF - enhanced binding energies
- Metal substitution seems to have a negligible effect on H₂ interactions.

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Application to adsorption of molecules on a surface

Influence of van der Waal's forces on the adsorption structure of organic molecules on silicon

[K. Johnston](#), J. Kleis, B. I. Lundqvist, R. Nieminen, *Phys. Rev.B* **77**, 121404 (2008)

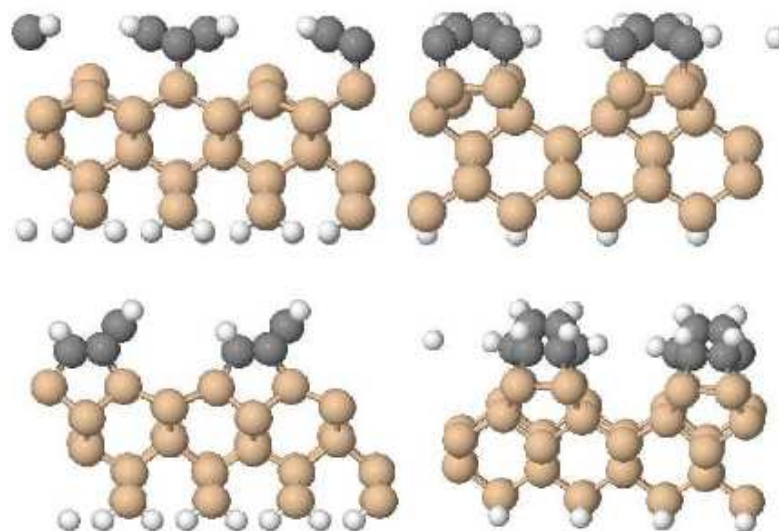


FIG. 1: (Color online) Butterfly (BF) (top), and tight-bridge (TB) (bottom) structures of C_6H_6 on $Si(001)-(2\times 1)$. LHS: viewed along $[\bar{1}10]$. RHS: viewed along $[110]$ dimer rows.