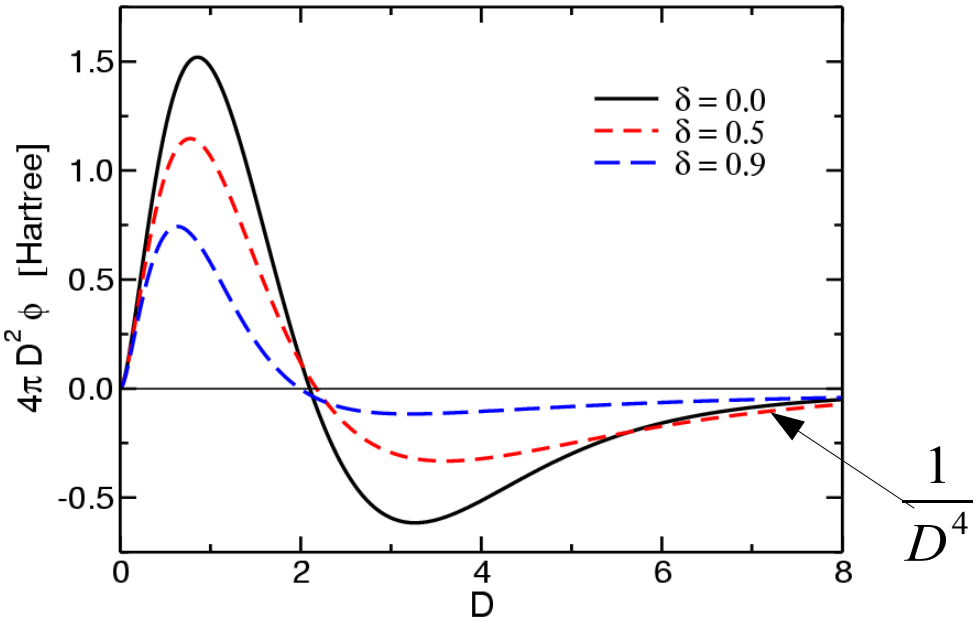
Form of our nonlocal correlation functional

$$E_c^{nl} = \frac{1}{2}\int d^3 r \int d^3 r' \, n(\vec{r})\,\phi(\vec{r},\vec{r}')\,n(\vec{r}')$$

$$where\ \phi(\vec{r},\vec{r}') = \phi(q(\vec{r})R, q(\vec{r}')R), \quad q(\vec{r}) = q\left(n(\vec{r}), \nabla n(\vec{r})\right)$$



$$D = \frac{q+q'}{2} R, \ where\ R = |r - r'|$$

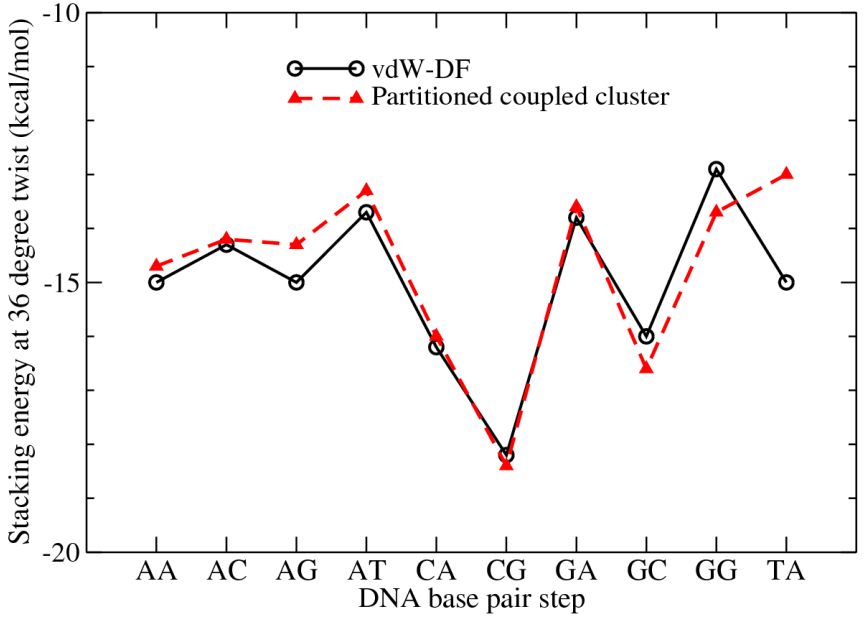
$$\delta = \frac{1}{2}\frac{q-q'}{q+q'}, where\ q = q(r),\ q' = q(r')$$

Integral over black curve vanishes, implying no contribution in local density approximation. Key to seamlessness and lack of double counting.

Strengths and weaknesses of the functional

- Predicted interaction energies of a rather wide range of large vdW systems comes out rather well (+)
- Predicted interaction energies of small vdW systems not so good (-)
- Shape of energy minima: good (+) but a little too shallow (-)
- Predicted equilibrium separations come out rather consistently (+) too large (-) by ~0.3 Å.
- It is a full density functional that works just like LDA or GGA in computer codes (+). Fully self-consistent calculations with geometry optimization (+).
- Some issues with metallic systems (-).

Comparison with best quantum chemical calculations for interaction between DNA base pair steps



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

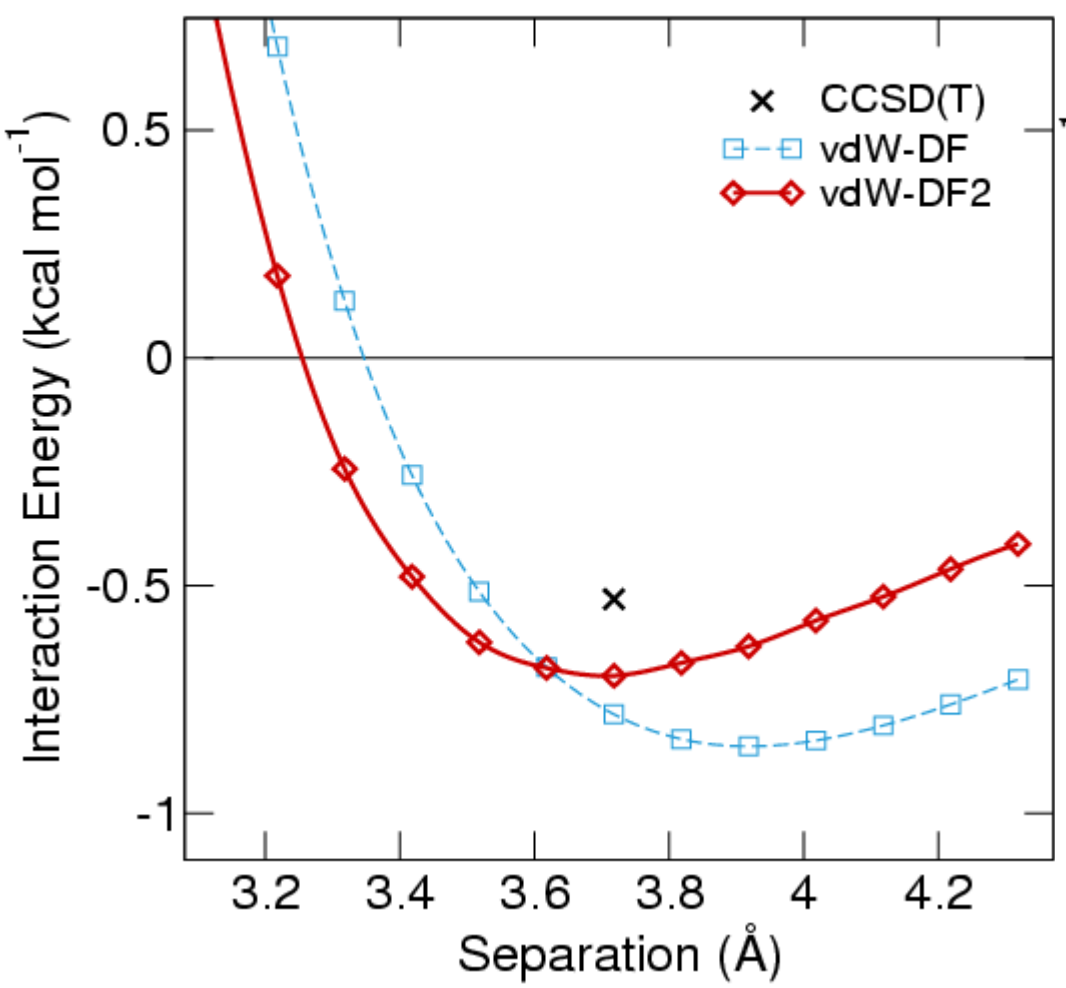
*Cooper, J. et al. JACS, 2008, **130**, 1304
Šponer, J. et al. *Chem. Eur. J.* **2006, *12*, 2854

Separation distance (rise) ~3.5 Å vs. ~3.3 Å from QC and experiment

Dispersion dominated duplexes in S22 set

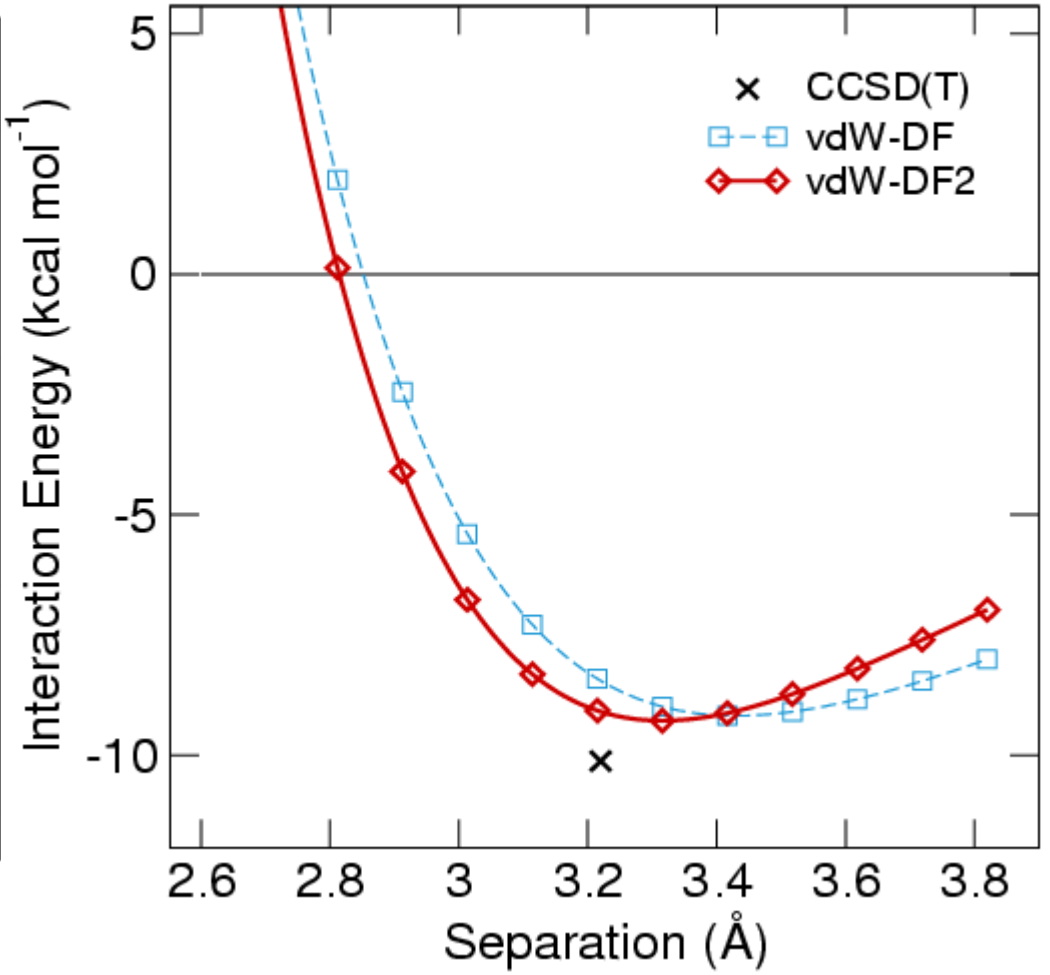
Worst case

CH_4 dimer



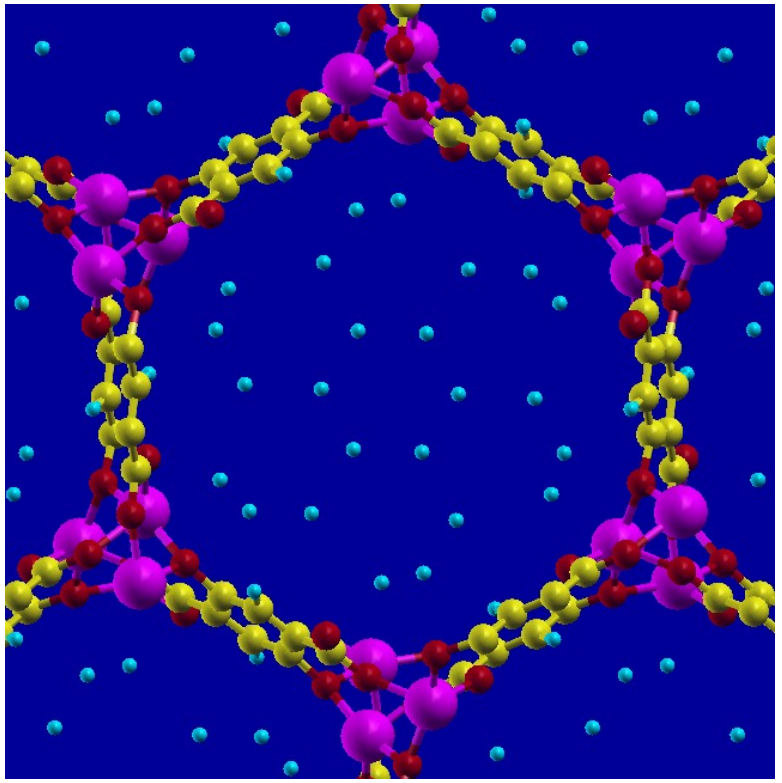
Typical case

Uracil dimer (stack)



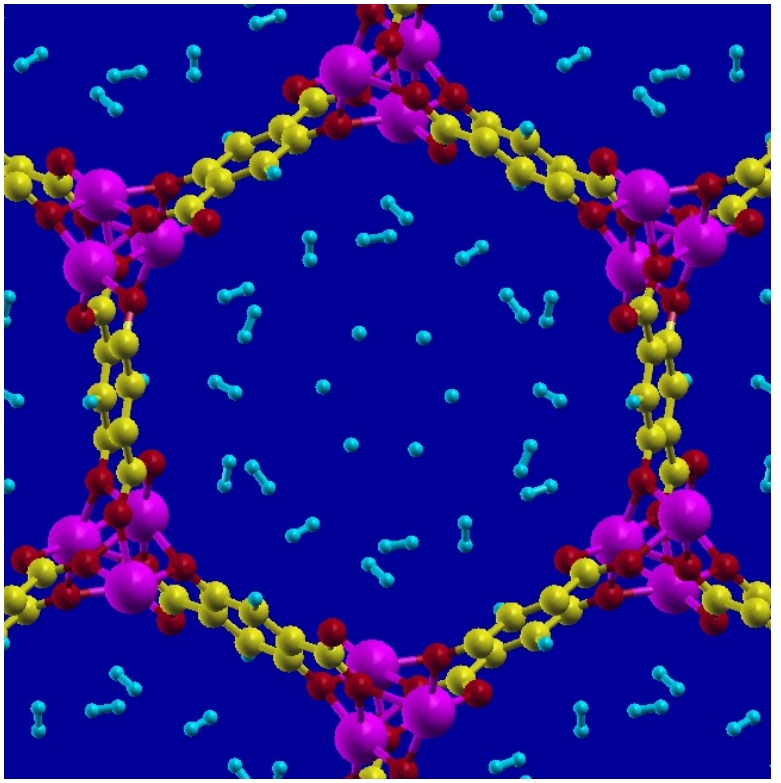
24 H_2 per cell in MOF-74

Experiment vs. theory



Neutron diffraction at 4K (D_2)

Y. Liu et al., Langmuir **24,** 4772 (2008)



vdW-DF

L. Kong et al., PRL **103**, 096103 (2009)

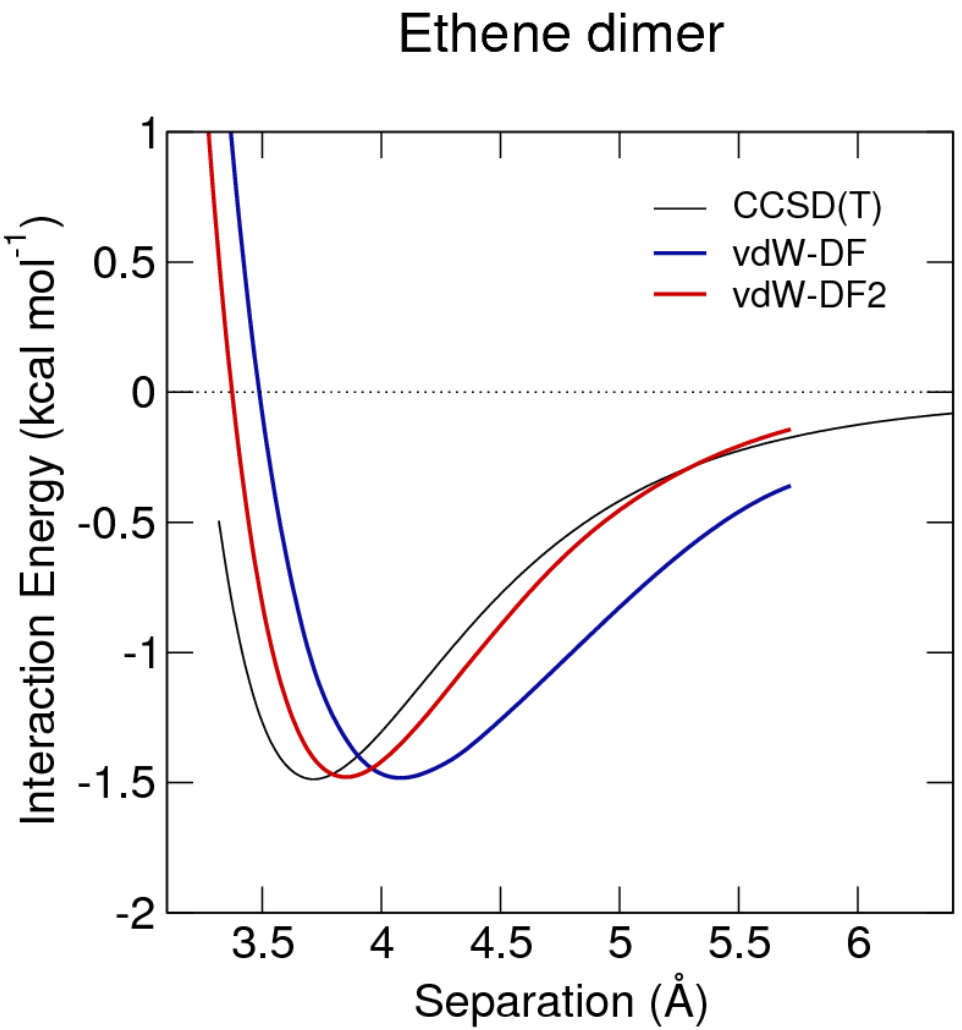
Note: the 24 H_2 are at 8 different depths

Binding energy of H_2 at Zn site

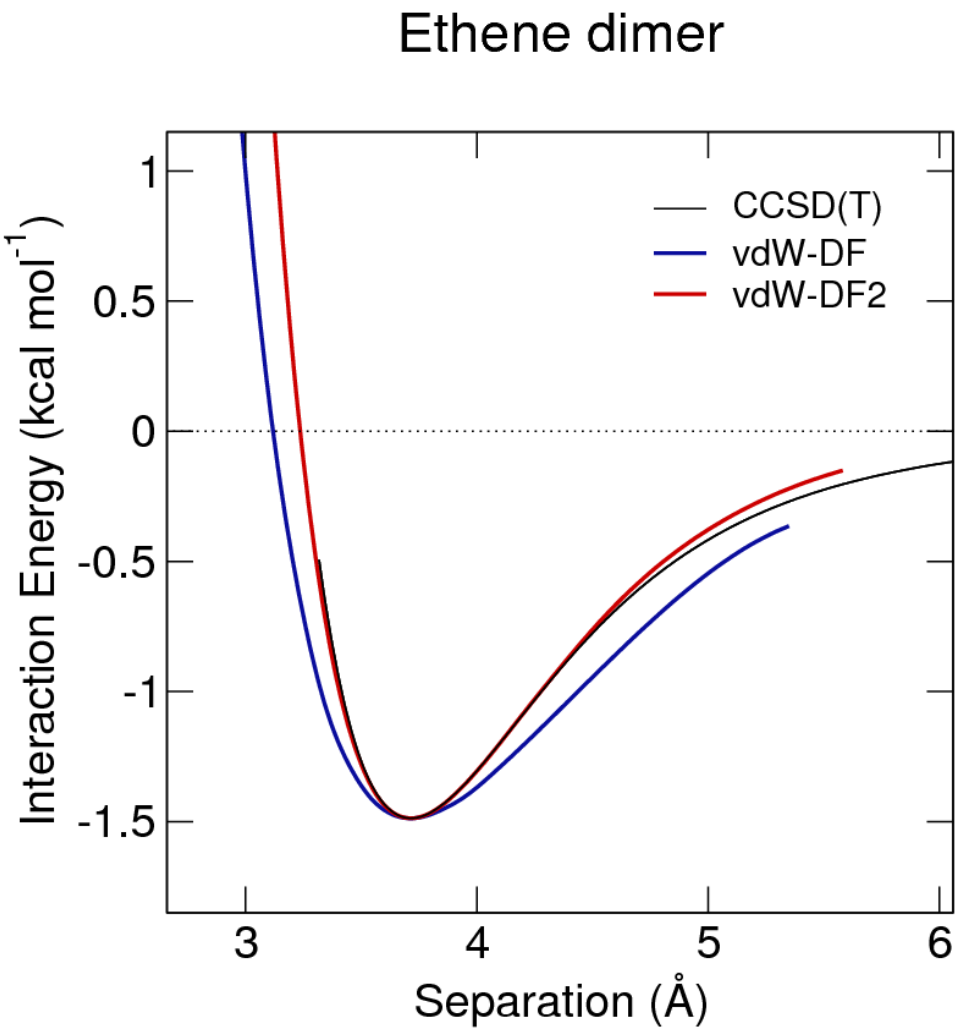
Experiment vs. theory

- Experiment
  - Q_{st} = 91 meV [Y. Liu et al., Langmuir **24,** 4772 (2008**)**]
  - Q_{st} = 88 meV [W. Zhou et al., JACS **130**,15268 (2008)]
- Theory
  - E_{GGA} = 46 meV (no zero point correction) [Zhou et al. (above)]
  - E_{LDA} = 230 meV (no zero point correction) [Zhou et al. (above)]
  - E_{vdW} = 130 meV(no zero point correction) [present work]
  - E_{vdW} = 100 meV (with zero point correction) [present work]

Shape of minimum



As calculated



Shifted to common minimum