Van der Waals interactions in DFT

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• KITP, Santa Barbara, November 2, 2009

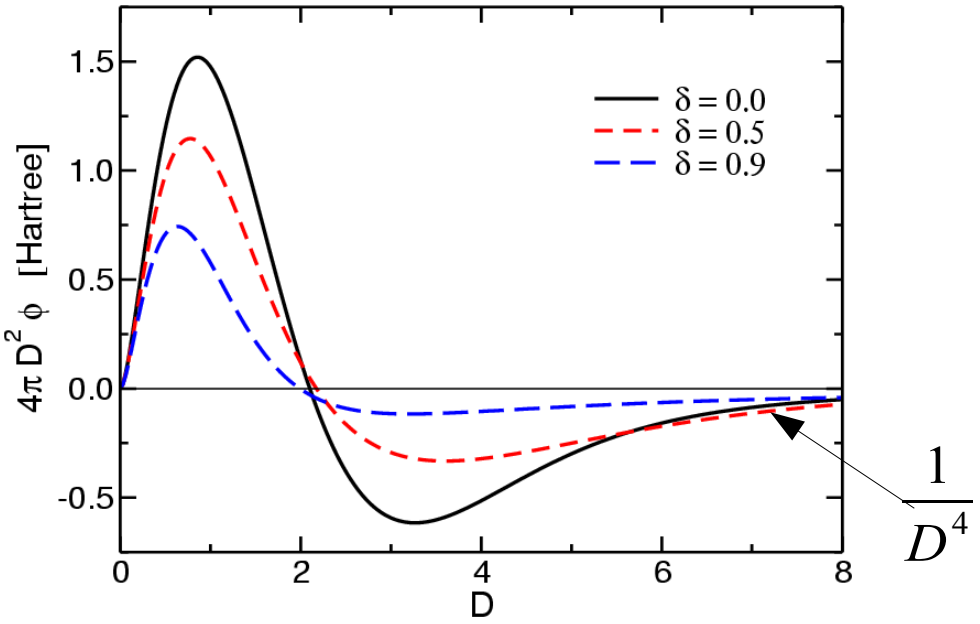
VdW-DF: Ingredients of the long-range (nonlocal) part of correlation functional

- Approximate single pole form for the density response function. Satisfying known limits, sum-rules, and invariances. Pole position scaled using exact electron-gas ground-state energy input, including the appropriate gradient correction. Pole residue from sum rule.
- Non-empirical. No fitted parameters.
- M. Dion et al., Phys. Rev. Lett. **92,** 246491 (2004).
- T. Thonhauser et al., Phys. Rev. B **76**, 125112 (2007). Includes fully self-consistent vdW contribution to V_{xc}.

Form of the nonlocal correlation functional

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

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



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

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

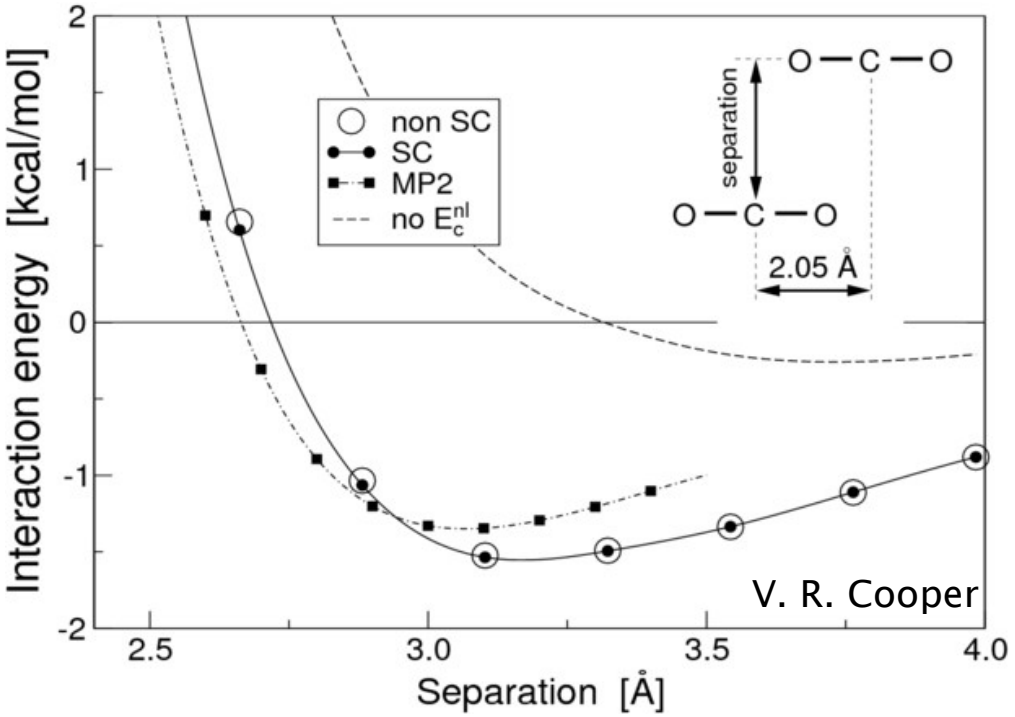
Integral over black curve vanishes, implying no contribution in local density approximation. Key to seamlessness and lack of double counting.

Self-consistent potential in vdW-DF

Comparison with post GGA perturbation of vdW-DF

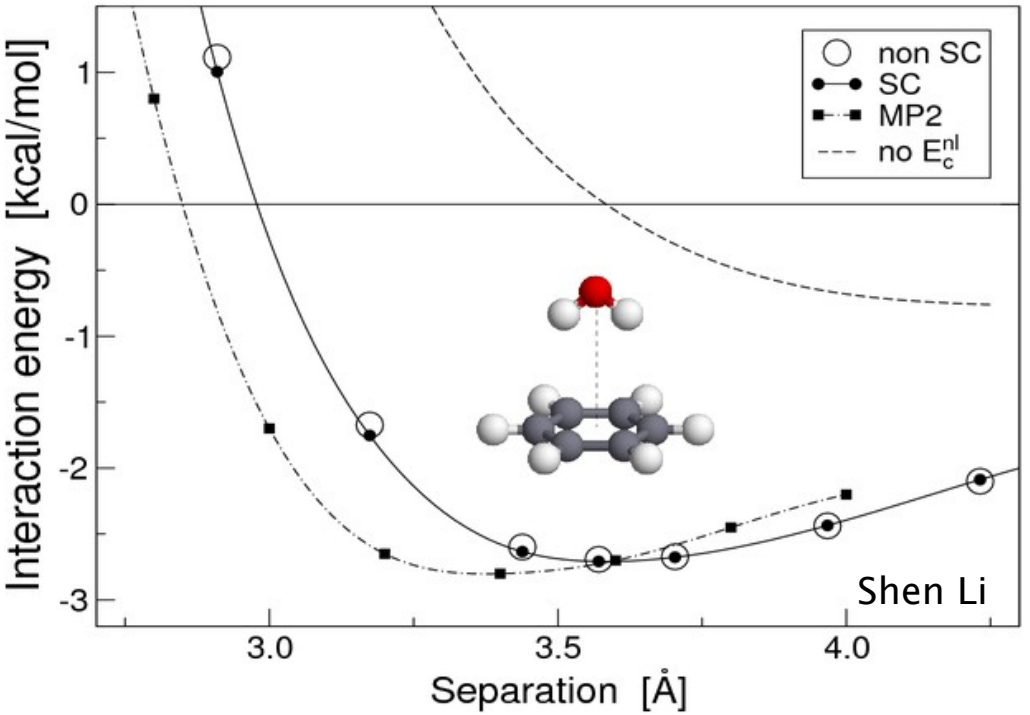
CO_2 dimer

VdW-DF Calculation by V. Cooper



Water on benzene

VdW-DF Calculation by Shen Li



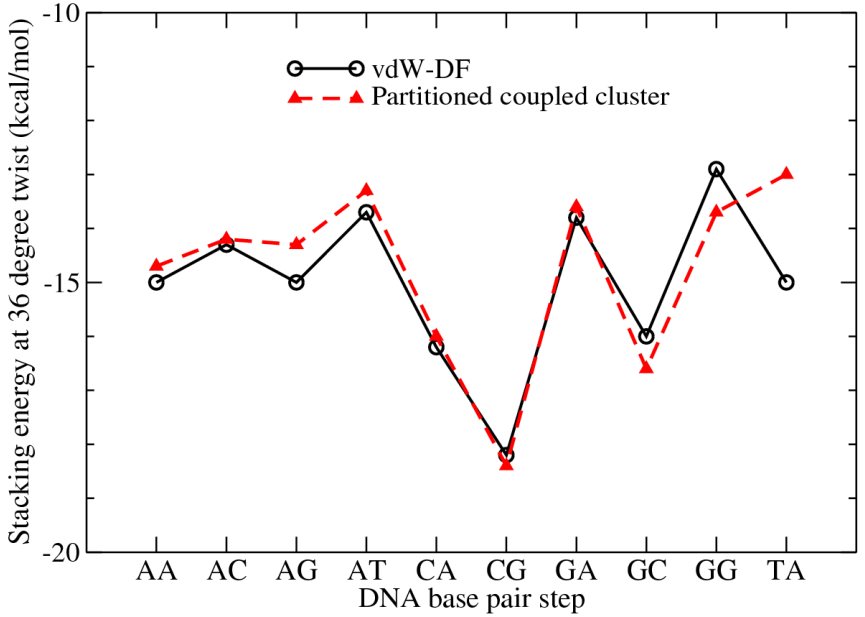
Post-process and self-consistent vdW-DF give about the same result near equilibrium separations. Differences at smaller separations.

Need self-consistent version for Hellmann-Feynman forces.

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 (-)
- Hydrogen bonds OK (+), but typically too weak (-)
- Shape of energy minima: good (+) but a little too shallow (-)
- Predicted equilibrium separations for vdW systems 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

Important recent development

- New algorithm for evaluating double integral in functional by G. Roman-Perez and J. Soler.
- Older method of direct integration requires N^2 operations. N is number of grid points where there is matter (vdW systems are sparse).
- New method uses a clever use of multiple fast fourier transforms, and requires M log M operations where M is the total number of grid points in the simulation cell.
- For large systems, the new method always wins, and we have found it to be extremely efficient. Even for small systems (~50 atoms) the efficiency difference between vdW and GGA is only ~2%. For 150 atom systems the time taken by vdW is immeasurably small. Timings with Abinit (self-consistent vdW added).

Implementations of Soler algorithm in public codes

- **Siesta** – full self-consistent implementation, including efficient forces, stress tensor, and vdW pseudopotential generation. Released in a developmental version of Siesta. Also released is a stand-alone vdW package for insertion in other codes. The latter released under a BSD license that allows modification and redistribution. http://www.icmab.es/siesta/
- **GPAW** – Independently coded version. Full self-consistent implementation. No stress tensor planned in near future. Uses PBE and revPBE PAW setups. https://wiki.fysik.dtu.dk/gpaw/

Efficient Implementation of a van der Waals Density Functional: Application to Double-Wall Carbon Nanotubes

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(Received 1 December 2008; published 27 August 2009)

We present an efficient implementation of the van der Waals density functional of Dion *et al.* [Phys. Rev. Lett. **92**, 246401 (2004)], which expresses the nonlocal correlation energy as a double spatial integral. We factorize the integration kernel and use fast Fourier transforms to evaluate the self-consistent potential, total energy, and atomic forces, in $O(N \log N)$ operations. The resulting overhead, for medium and large systems, is a small fraction of the total computational cost, representing a dramatic speedup over the $O(N^2)$ evaluation of the double integral. This opens the realm of first-principles simulations to the large systems of interest in soft matter and biomolecular problems. We apply the method to calculate the binding energies and the barriers for relative translation and rotation in double-wall carbon nanotubes.

DOI: 10.1103/PhysRevLett.103.096102 PACS numbers: 61.46.Fg, 31.15.eg, 71.15.−m

Energetics and Dynamics of H_2 Adsorbed in a Nanoporous Material at Low Temperature

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(Received 30 June 2009; published 27 August 2009)

Molecular hydrogen adsorption in a nanoporous metal-organic framework structure (MOF-74) is studied via van der Waals density-functional calculations. The primary and secondary binding sites for H_2 are confirmed. The low-lying rotational and translational energy levels are calculated, based on the orientation and position dependent potential energy surface at the two binding sites. A consistent picture is obtained between the calculated rotational-translational transitions for different H_2 loadings and those measured by inelastic neutron scattering exciting the singlet to triplet (para to ortho) transition in H_2. The H_2 binding energy after zero-point energy correction due to the rotational and translational motions is predicted to be -100 meV in good agreement with the experimental value of -90 meV.

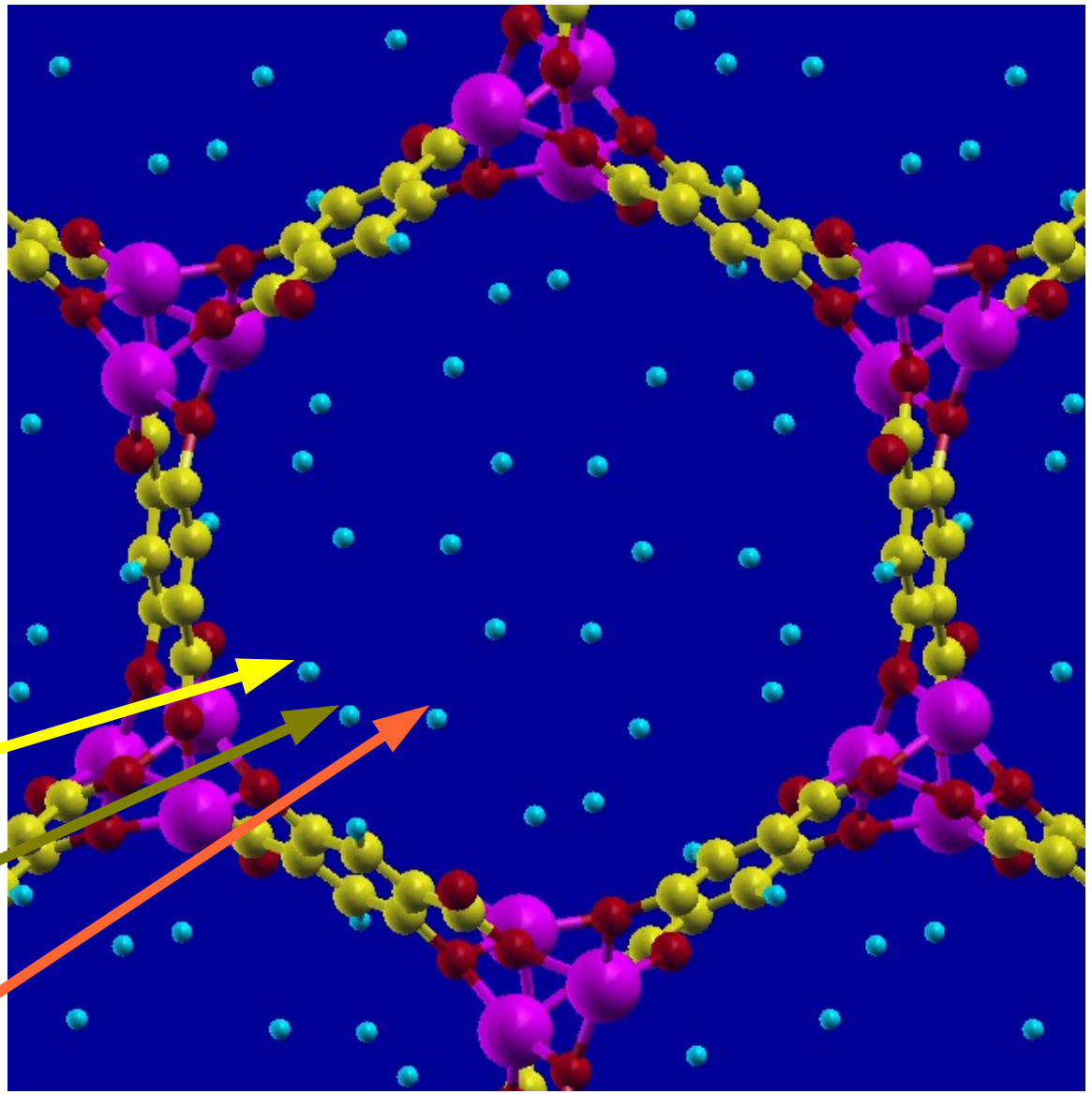
DOI: 10.1103/PhysRevLett.103.096103 PACS numbers: 68.43.Bc, 68.43.Fg, 84.60.Ve

Hydrogen molecules in nanoporous materials

- I will talk about the following to illustrate the usefulness of the Soler Algorithm:
  - MOF-74: recent neutron diffraction results explained using vdW-DF. L. Kong *et al.*, Phys. Rev. Lett. **48**, 7165 (2009).
  - RPM-3 (Rutgers Porous Material – 3). Fabricated by Jing Li. High heat of sorption, both experiment and vdW-DF. A. Lan *et al.*, Inorg. Chem. **48**, 7165 (2009).

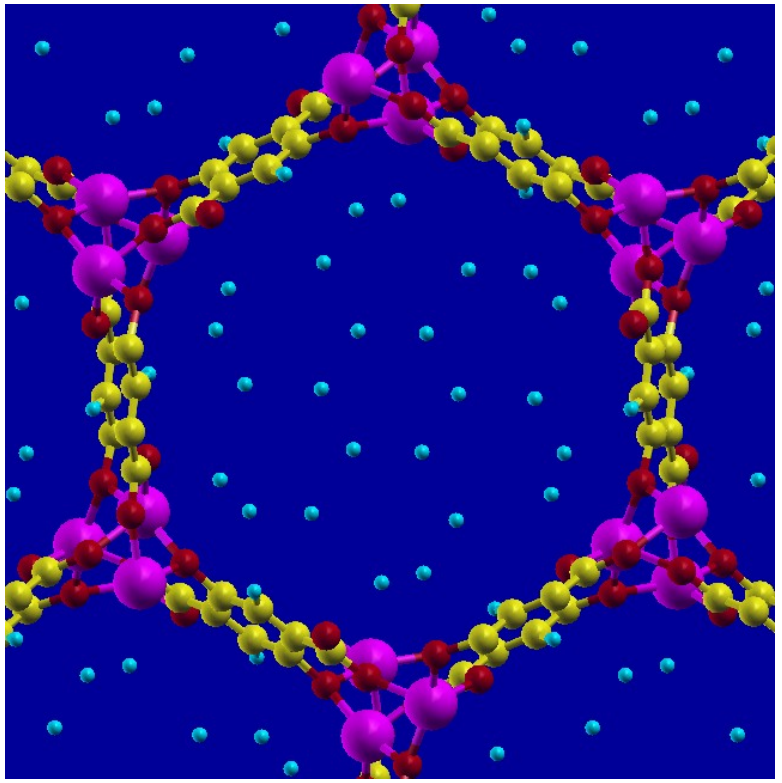
Binding sites of H_2 in MOF-74

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



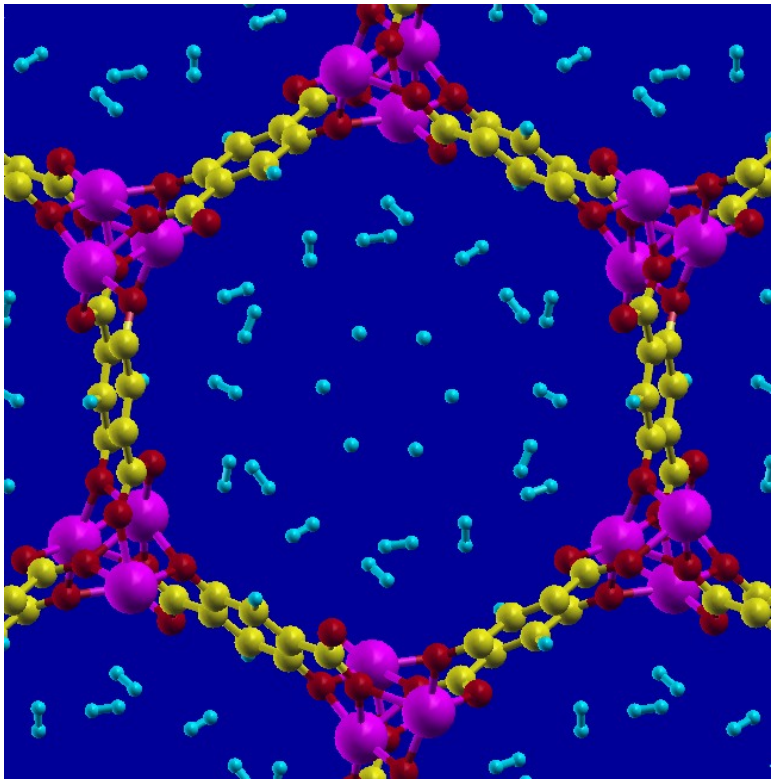
24 H_2 per cell in MOF-74

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)

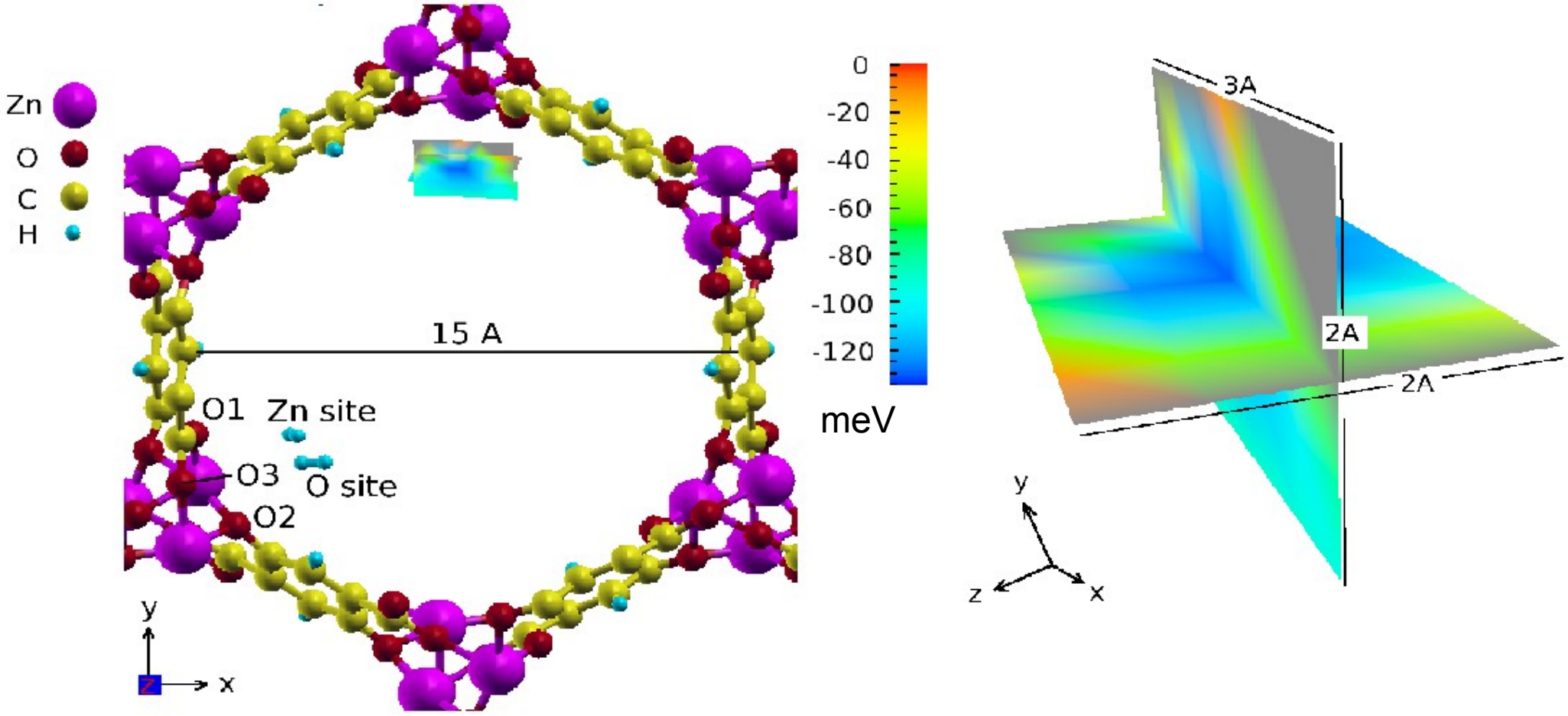
Note: the 24 H_2 are at 8 different depths

Binding energy of H_2 at Zn site

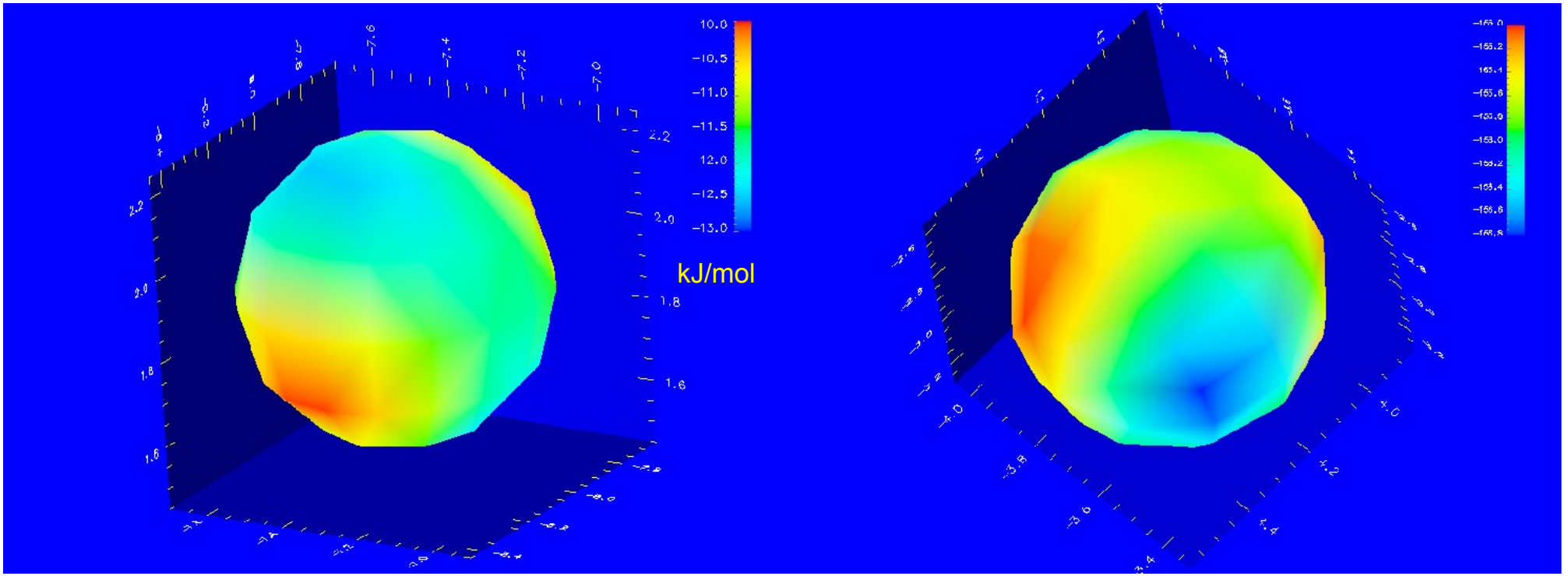
Experiment vs. theory

- 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]

Energy map near Zn site



Rotational energy maps

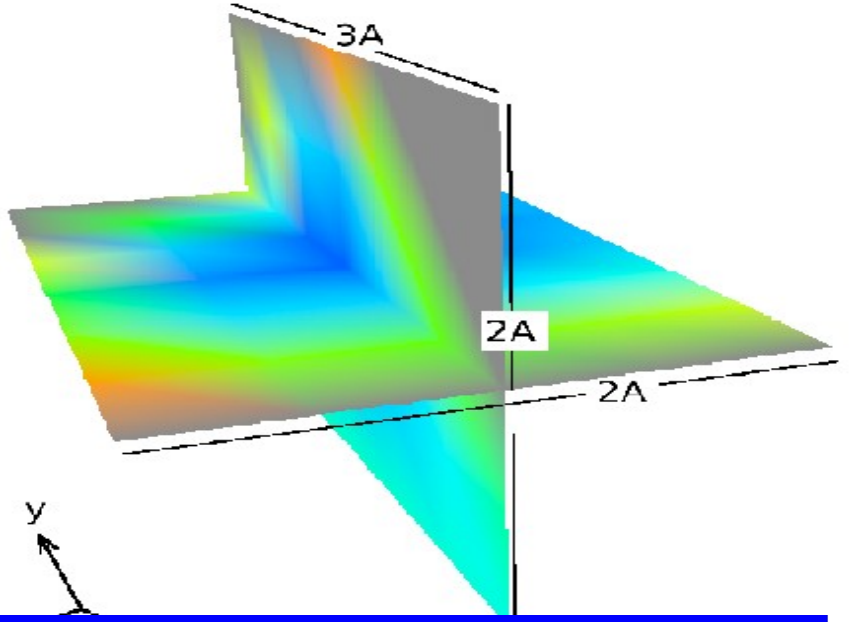


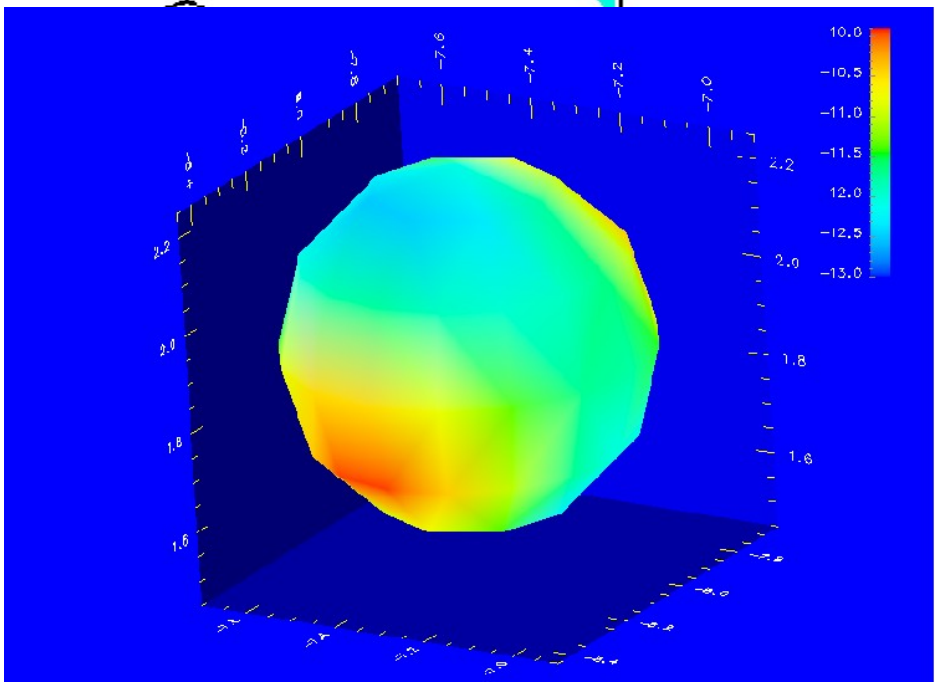
Zn site

O site

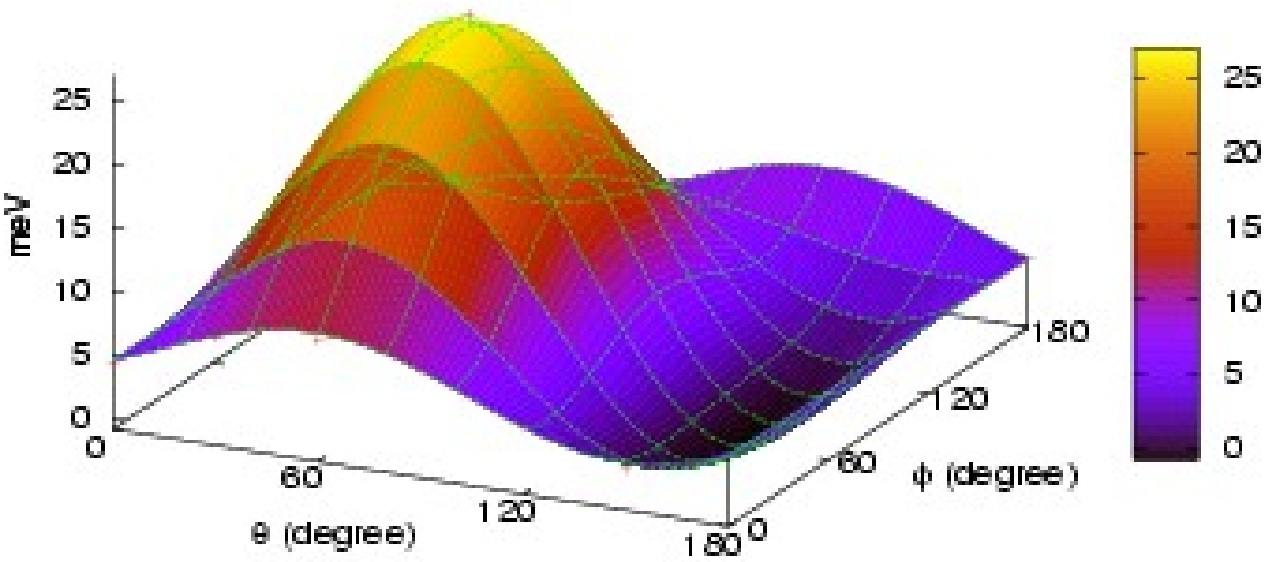
Calculation of zero point energies from first principles

- Frustrated translations
  - Map translational potential
  - Solve Schrödinger eq.
  - Get ZP of ~20 meV
- Frustrated rotations
  - Map angular potential
  - Solve Schrödinger eq.
  - Get ZP of ~10 meV
- Net zero point = ~30 mdV

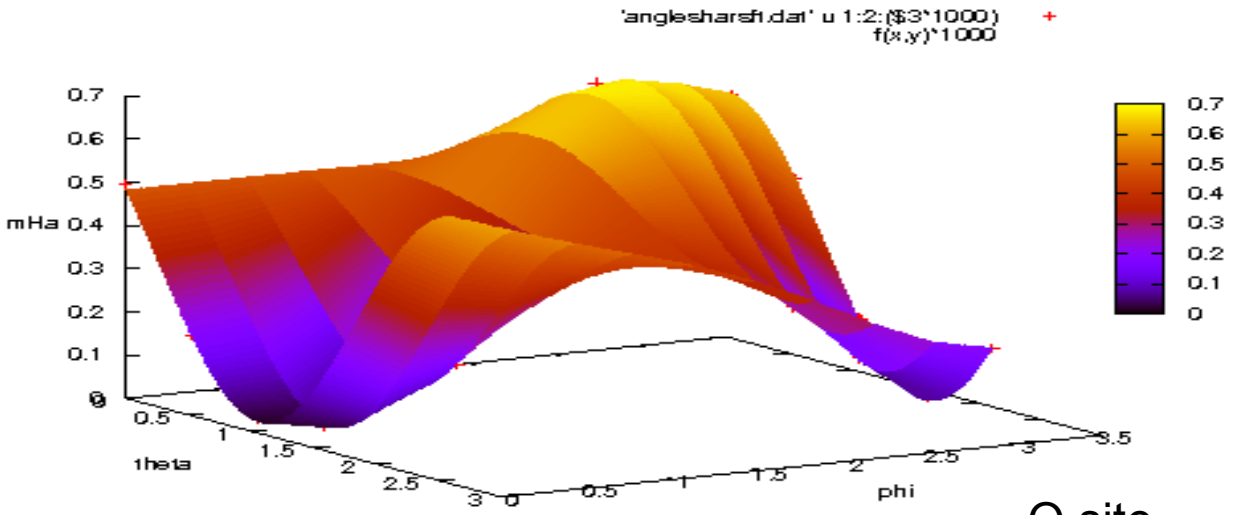




Spherical harmonic fits for solving rotational Schrödinger equation



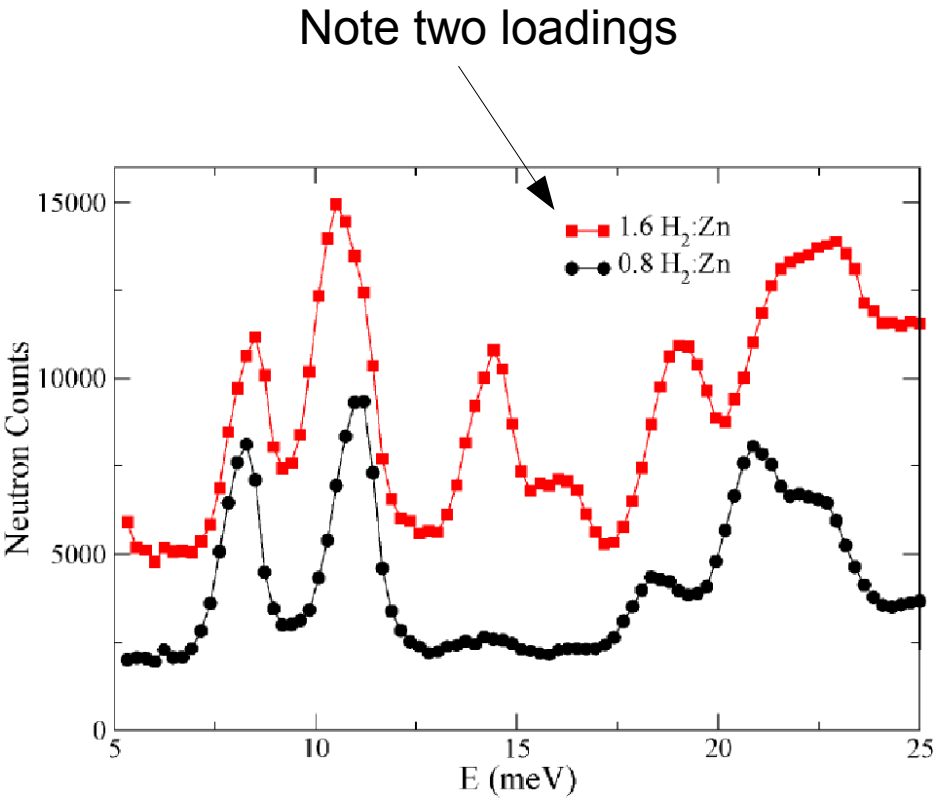
Zn site



O site

Rotational structure via inelastic neutron scattering off H_2 in MOF-74

- Experiment by Y. Liu et al., Langmuir **24,** 4772 (2008**).**
- Start with 100% para H_2 (ground state singlet) at 4K.
- Neutron excites H_2 to the ortho excited state triplet, now split.
- Frustrated translation sidebands also appear.
- Energy loss structure varies with H_2 loading.
- Can we predict this ab initio?

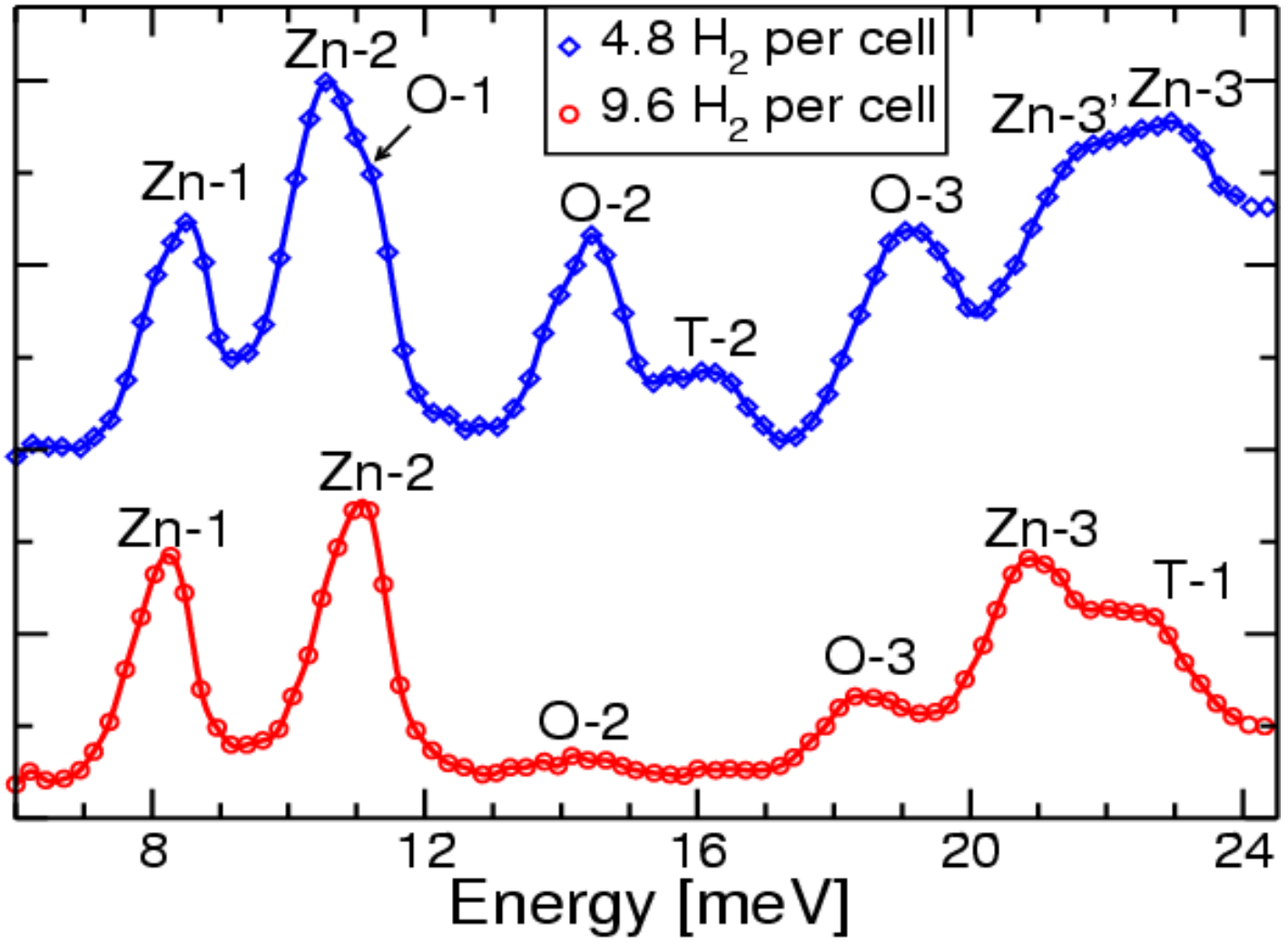


Black curve: most H_2 at Zn sites

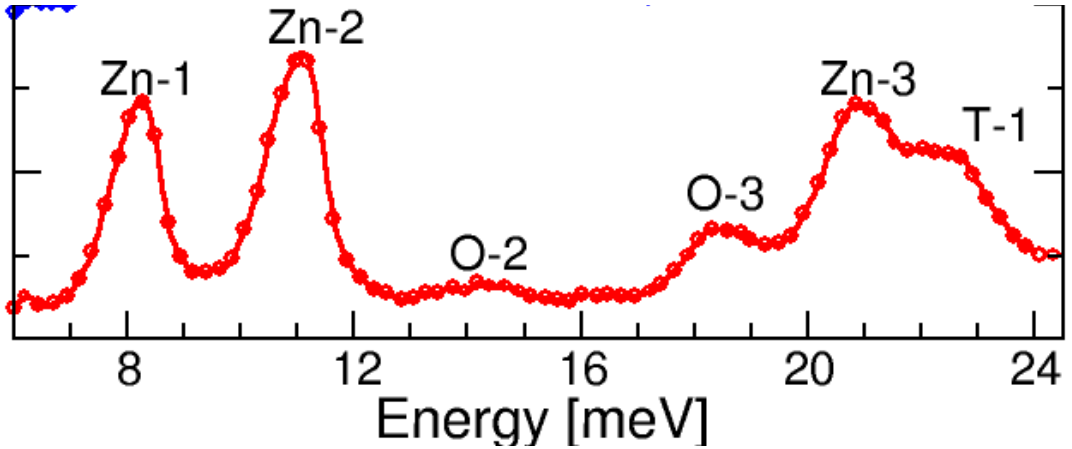
Red curve: H_2 at both Zn and O sites

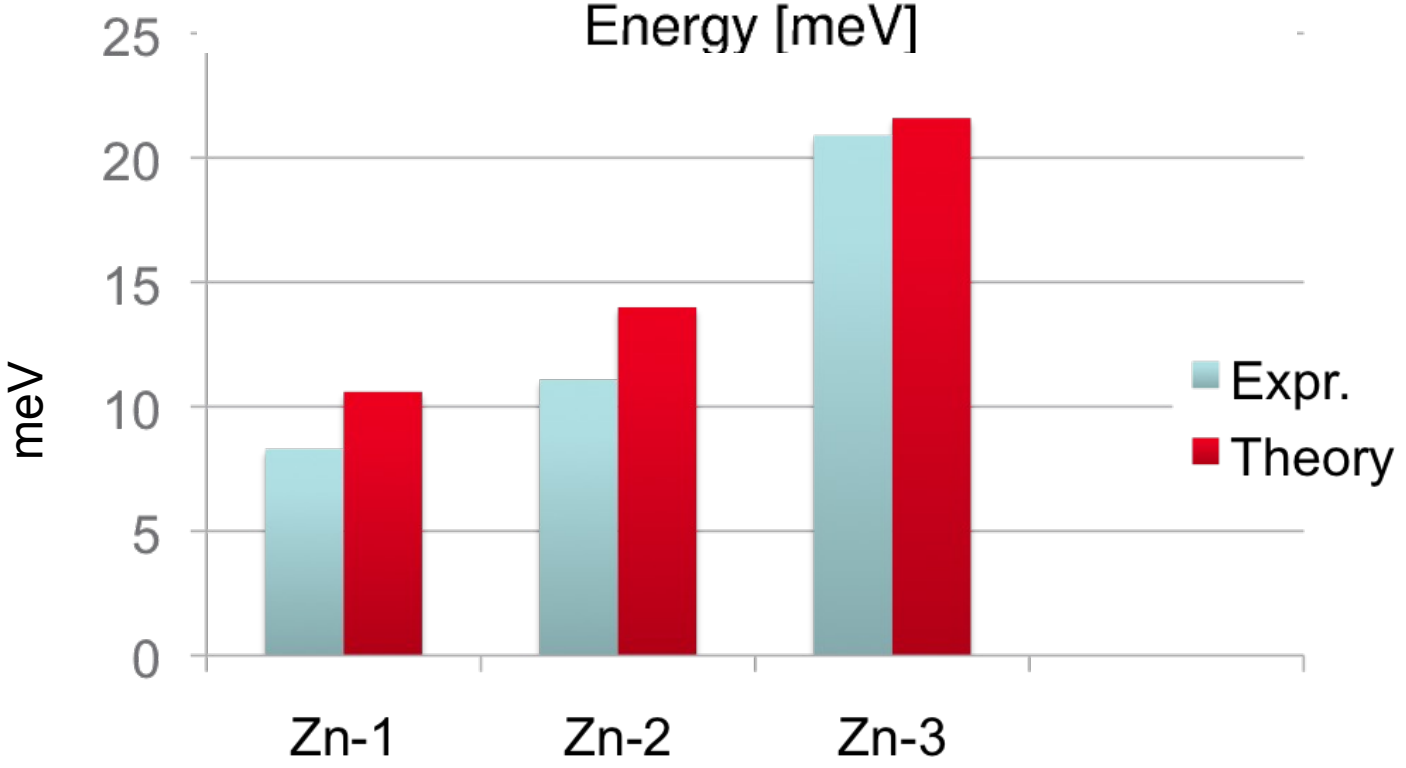
Our neutron scattering peak assignments based on our calculations

All rotational peaks would be at 14.7 meV in the absence of a rotational potential



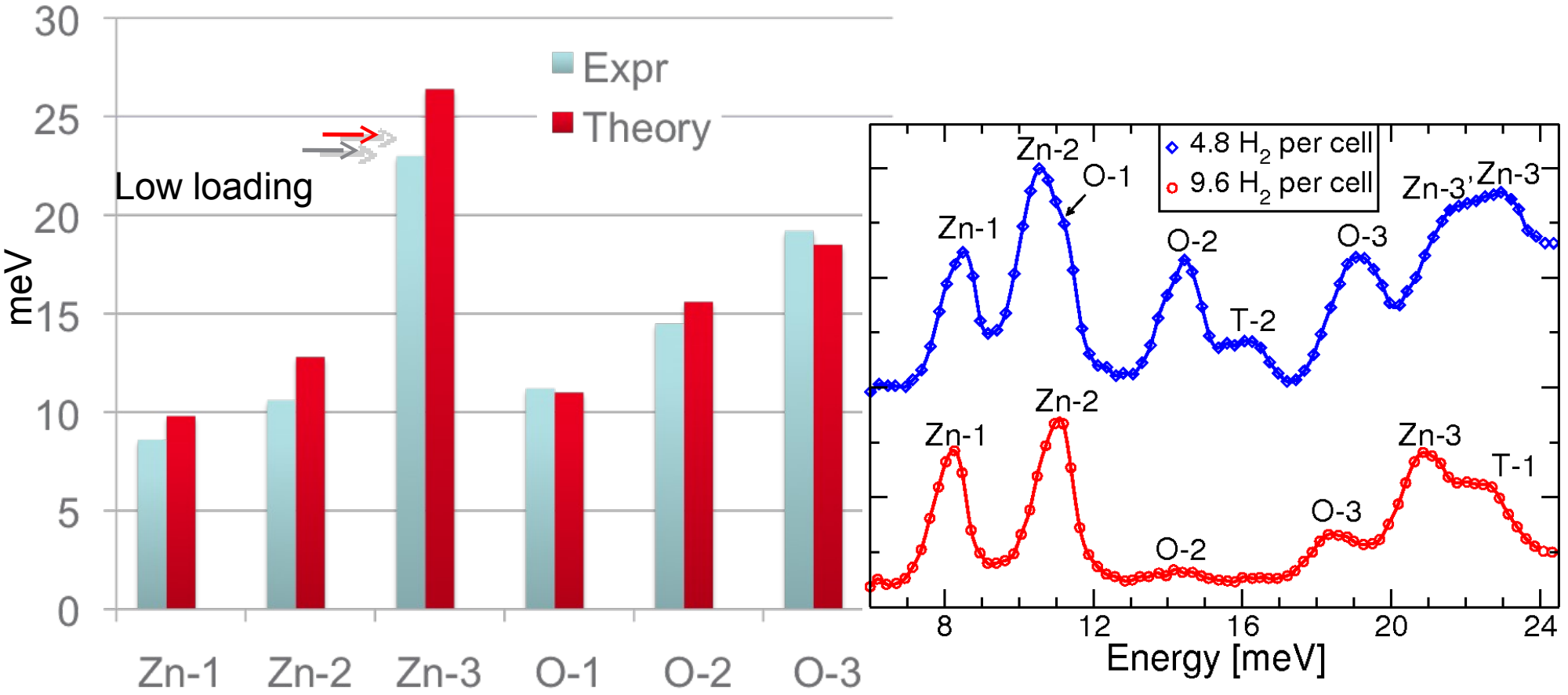
Para-ortho excitation of H_2 in MOF-74(low loading)





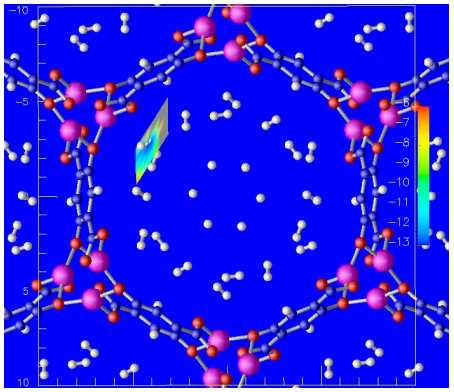
Kong et al. PRL 103 (2009); Expr: Liu et al. Langmuir 24 (2008)

Para-ortho excitation of H_2 in MOF-74(high loading)



Kong et al. PRL 103 (2009); Expr: Liu et al. Langmuir 24 (2008)

Summary - MOF-74

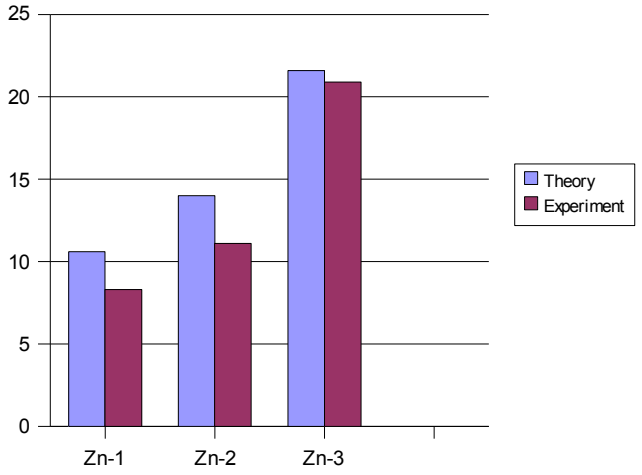


Ab initio prediction of sites with qualitative agreement with neutron scattering measurements by others

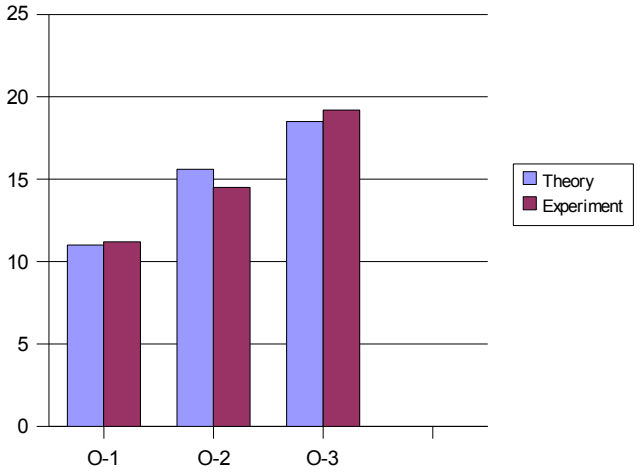
Binding energy ab initio theory by us:
100 meV which includes -10 meV zero point from frustrated rotations and -20 meV from frustrated translations.

Binding energy experiment by others:
90 meV

Low loading energy loss in meV



Higher loading energy loss in meV



Ab initio prediction of rotational excitation energies at different loadings, in qualitative agreement with inelastic neutron scattering.

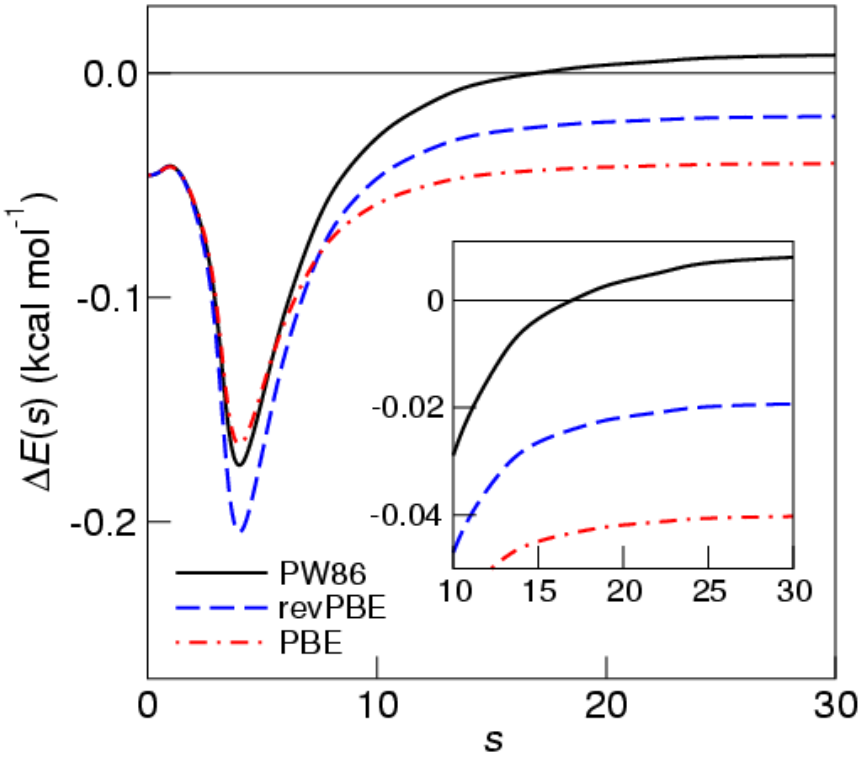
What's in store for improvements?

- Want to improve intermonomer spacing issue as well as energies.Two approaches:
  - Develop a better exchange functional to match the present vdW-DF. Valentino Cooper – preprint
  - Develop an exchange functional to match HF, then improve vdW-DF to work with HF.
    - **Exchange functional:** Kanneman & Becke found that PW86 worked best interaction between rare gas atoms. Murray, Lee, & Langreth (JCTC, DOI: /10.1021/ct900365q) (Sept. 2009) found the same for small molecules (less than 30 atoms total).
    - **Correlation functional:** VdW-DF for use with HF or PW86 in progress.

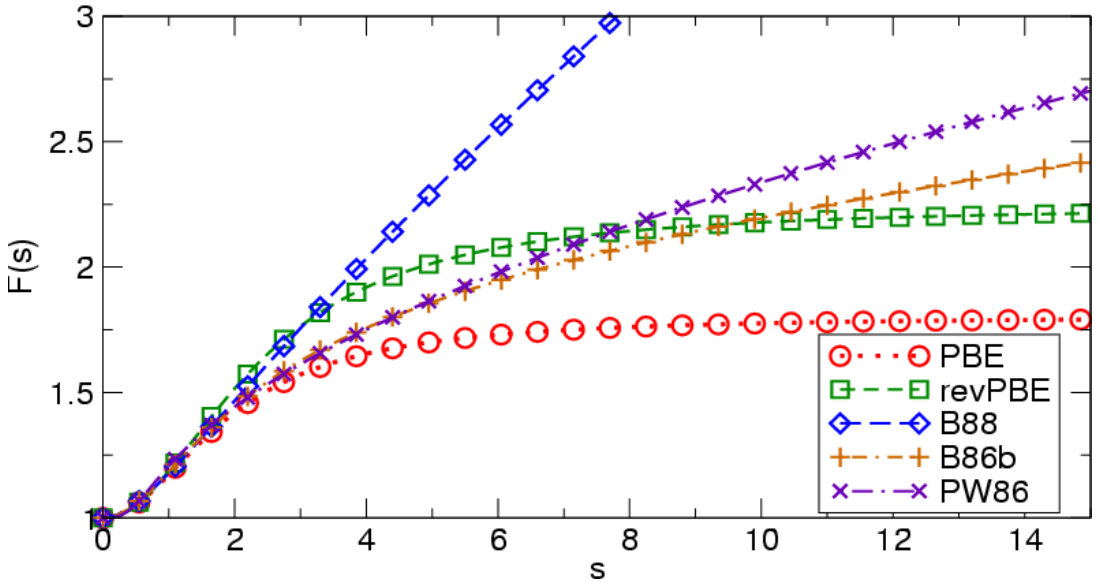
Exchange: enhancement factor analysis

To right: contributions to the gradient dependent part of the exchange interaction energy of a crossed H_2 dimer at a separation of 4 Å. Ordinate shows the sum over all spatial points with values of s less than the s given in the abscissa.

Below: enhancement factors F(s) for exchange functionals tested.



E. Murray et al. JCTC 2009



s = reduced gradient = $|\text{grad } n|/2k_F n$

F(s) = factor times which the magnitude of the LDA exchange is enhanced

Spurious exchange binding between fragments in LDA

J. Harris, Phys. Rev. B **31**, 1770 (1985)

The issue of this spurious exchange binding has been studied previously by Harris[51] in the case of two interacting He atoms. In examining the system in terms of the first order change in the potential due to the overlap in the densities:

Overlap M

$$M = \int d^3r\, \psi_{He}(\mathbf{r}-\mathbf{R}_1)\, \psi_{He}(\mathbf{r}-\mathbf{R}_2), \tag{2}$$

where $\mathbf{R}_1$ and $\mathbf{R}_2$ are the nuclear locations and

$$\psi_{He}(\mathbf{r}) = \frac{1}{\sqrt{2}} n^{1/2}(\mathbf{r}). \tag{3}$$

He noted that the leading contribution to the change in the energy comes from competition between the kinetic term and the exchange-correlation term. In Hartree-Fock, both the kinetic term, which is repulsive, and the exchange term, which is attractive, are proportional to M^2. This yields an interaction energy which is monotonic in $|\mathbf{R}_1 - \mathbf{R}_2|$ and always repulsive, and which may be written schematically as

In HF, T and E_x have same dependence on overlap M

$$\delta E \simeq (C_T^{HF} - C_x^{HF}) M^2. \tag{4}$$

However, in the case of LDA, the exchange term is proportional to $M^{4/3}$, leading to a situation where LDA can yield an attractive interaction for small overlaps (small values of M), so that Eq. (4) is replaced by

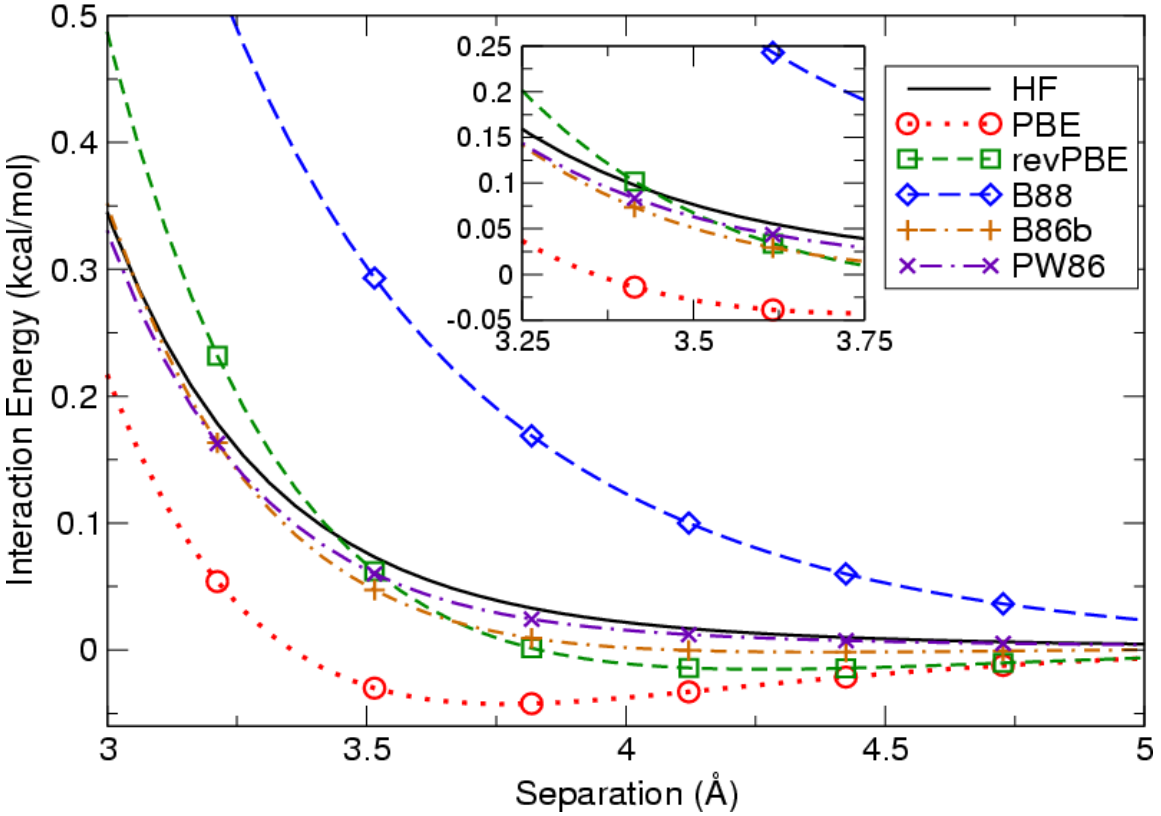
In LDA, exchange dominates.
Spurious binding from exchange.

$$\delta E \simeq C_T M^2 - C_x M^{4/3}. \tag{5}$$

GGAs can fix spurious LDA exchange attraction, but ...

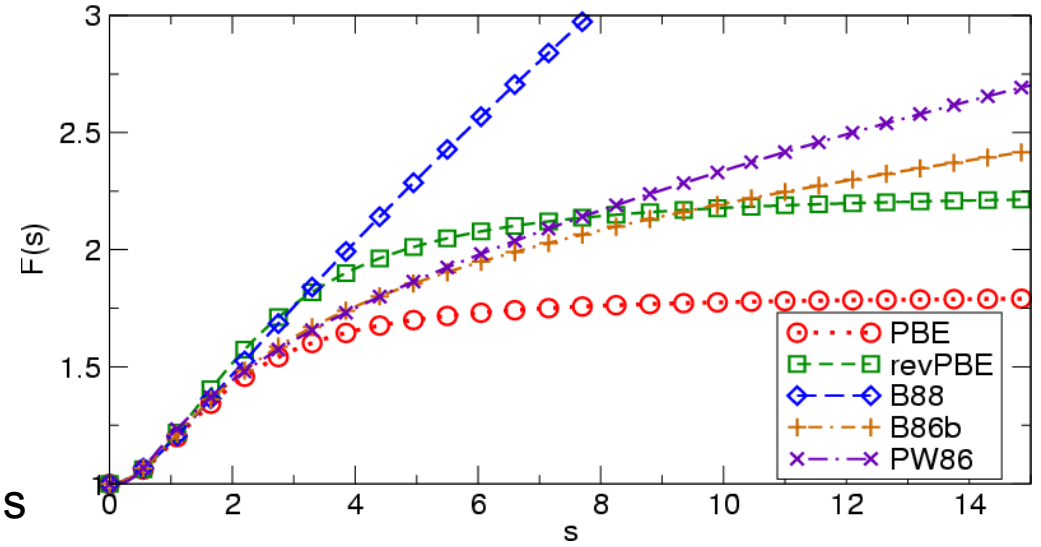
- GGAs for exchange can cancel the spurious LDA exchange binding.
- This can happen if the enhancement factor is increasing sufficiently rapidly with s, because overlap decreases s, giving repulsion.
- However, if the enhancement factor turns flat at large s [as for PBE and revPBE (also Becke86a, which is not considered here)], then the spurious LDA exchange repulsion can be exacerbated, not canceled, because one is effectively left with an LDA like region with a larger $|e_x|$.

HF vs. GGA functionals for crossed H_2



E. Murray et al.
JCTC (2009)

Note: for many fragments we studied, PBE is not this bad, and often revPBE is worse. All in all, though, PW86 wins, with B86b a close second. Enhancing earlier conclusion of Kanneman & Becke JCTC 2009, for rare gas atoms



S22

- Twenty-two prototypical small molecular complexes for non-covalent interactions in biological molecules
  - Hydrogen bonded
  - Dispersion dominated
  - Mixed
- The most accurate quantum chemical calculation results are available

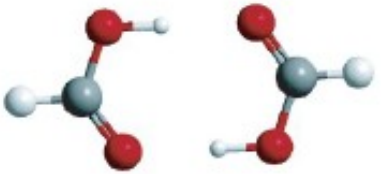
Petr Jurecka, Jirí Sponer, Jirí Cerný, and Pavel Hobza,
Phys. Chem. Chem. Phys. **8**, 1985 (2006).

Laszlo F. Molnar, Xiao He, Bing Wang, and Kenneth M. Merz,
J. Chem. Phys. **131**, 065102 (2009).

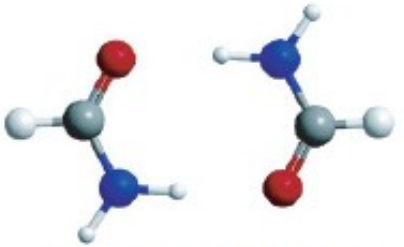
Hydrogen-bonded complexes

(1) Ammonia dimer

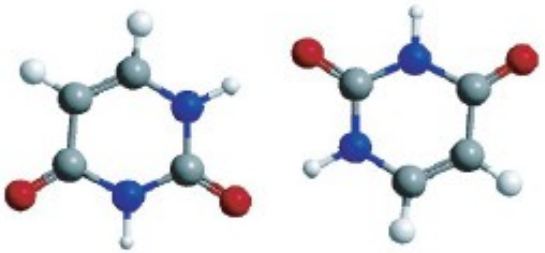
(2) Water dimer



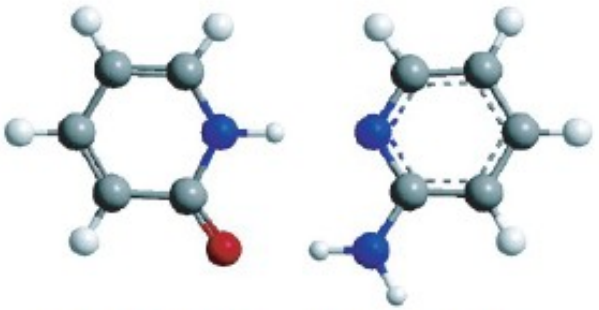
(3) Formic acid dimer



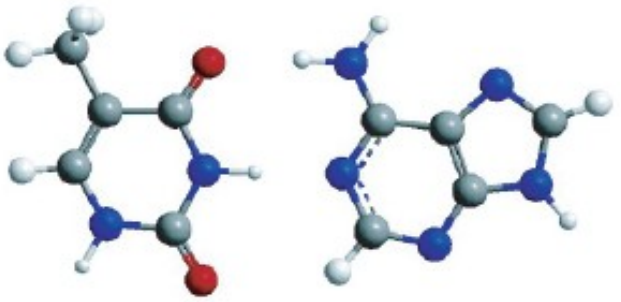
(4) Formamide dimer



(5) Uracil dimer



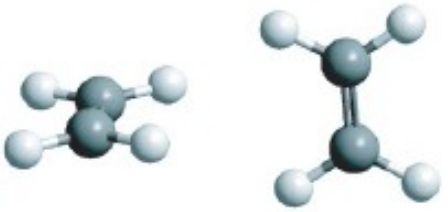
(6) 2-pyridoxine · 2-aminopyridine



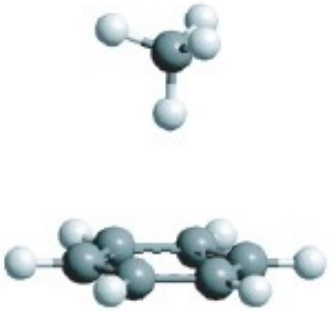
(7) Adenine · thymine

Dispersion-dominated complexes

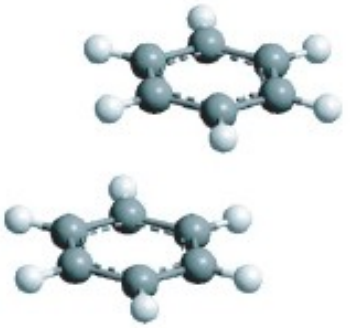
(8) Methane dimer



(9) Ethene dimer

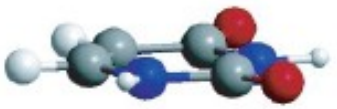


(10) Benzene · methane



(11) Benzene dimer

(12) Pyrazine dimer

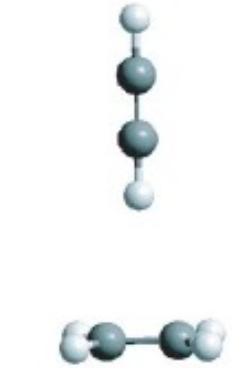


(13) Uracil dimer

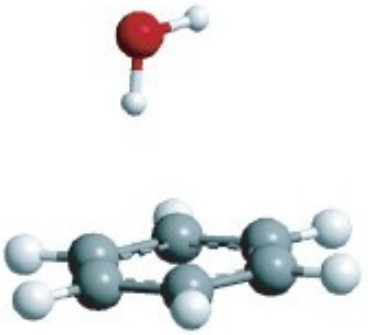
(14) Indole · benzene

(15) Adenine · thymine stack

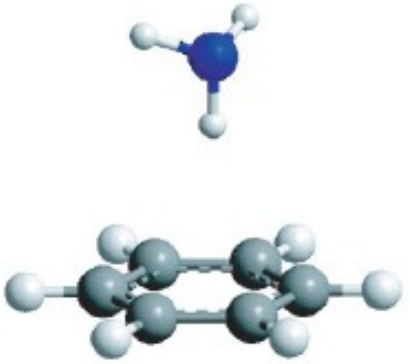
Mixed complexes



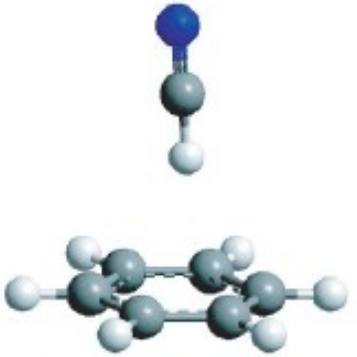
(16) Ethene · ethine



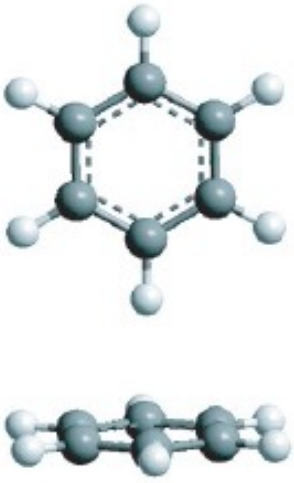
(17) Benzene · water



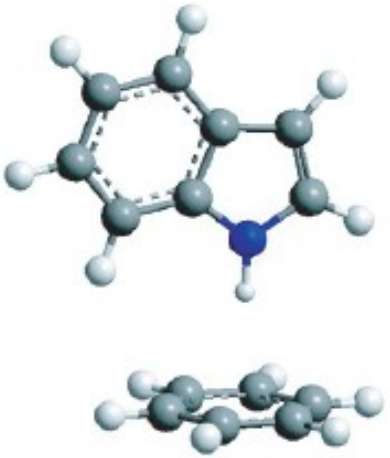
(18) Benzene · ammonia



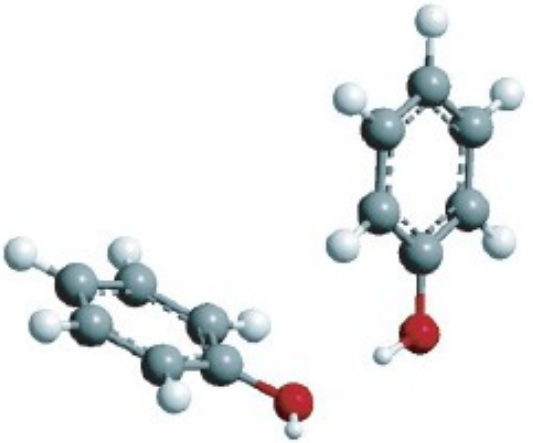
(19) Benzene · HCN



(20) Benzene dimer (T-shape)



(21) Indole · Benzene (T-shape)



(22) Phenol dimer

Tests on the S22 set

In the following slides I illustrate the behavior of the original vdW-DF alongside a developmental version labeled vdW-DF2. The original uses revPBE exchange, while the developmental version uses PW86 exchange, the form that best mimics HF exchange.

Calculations by Kyuho Lee

The first tests of vdW-DF on the S22 set were made by A. Gulans et al., PRB 2009

The slides from here on contain unpublished data and should be omitted from KITP web versions

Concluding remarks

- The method now requires negligibly more computing resources than GGA.
- The method shows promise to extend the broad successes of density functional theory to new classes of matter. You should use it.
- Many aspects of the functional can be improved, and we and other groups are working on this.