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

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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 $\rho$
  - 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*
Correlated spontaneous and induced dynamic fluctuations in electron distribution can result in net Coulomb interactions.
The vdW-DF

\[ E[\rho] = E_{\text{ion}}[\vec{R}_i] + T_S[\rho] + E_H[\rho] + \int V_{\text{ext}}(\vec{r}) \rho(\vec{r}) d^3\vec{r} + E_{\text{xc}}[\rho] \]

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

\[ E_c[\rho] = E_{c}^0[\rho] + E_{c}^{\text{nI}}[\rho] \]

(LDA)

The vdW-DF

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

No adjustable parameters!

\[ \Phi(\delta, D) = \frac{1}{2} \frac{(q - q')}{(q + q')}, \]

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

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

True non-local density functional!

\[ E_{\text{xc}}[\rho] = E_{\text{X}}^0[\rho]_{\text{(revPBE)}} + E_{\text{C}}^0[\rho]_{\text{(LDA)}} + E_{\text{C}}^{\text{nl}}[\rho] \]

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

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.

Thonhauser, Cooper, Li, Puzder, Hyldgaard and Langreth, PRB, 76, 125112, (2007)
### vdW-DF and petascale computing

<table>
<thead>
<tr>
<th>System</th>
<th># e⁻ (atoms)</th>
<th># grid pts.</th>
<th>revPBE</th>
<th>vdW-DF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pair</td>
<td>98 (30)</td>
<td>45431</td>
<td>73 min</td>
<td>40 min</td>
</tr>
<tr>
<td>Base pair step</td>
<td>196 (60)</td>
<td>89044</td>
<td>350 min</td>
<td>175 mins</td>
</tr>
</tbody>
</table>

*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 $\Theta(N^3)$ 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
Stacking interactions and the Twist of DNA
A brief description of DNA

- Adenine
- Thymine
- Guanine
- Cytosine
- Uracil

RNA
Research has shown:
- Transcription and replication
- Interaction of DNA with proteins and viruses
- Intercalation of chemotherapy drugs alter the structure of DNA

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

- Drug development
- Gene therapy
- Understanding mutations
- Genetic disorders
Are vdW interactions necessary?

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

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

Stacking interactions of nucleic acids

Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, JACS, 130, 1304, (2008)
\[ \Delta E \text{ vs. rotation angle} \]


Cooper, Thonhauser and Langreth JCP, 128, 204102 (2008)
### S22 data set

<table>
<thead>
<tr>
<th>System</th>
<th>vdw-DF</th>
<th>QC</th>
<th>BLYP-D (04)</th>
<th>BLYP-D (07)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT (WC)</td>
<td>-15.20</td>
<td>-16.37</td>
<td>-15.01</td>
<td>-17.19</td>
</tr>
<tr>
<td>Benzene-CH$_4$ (C$_3$)</td>
<td>-1.57</td>
<td>-1.50</td>
<td>-0.90</td>
<td>-1.37</td>
</tr>
<tr>
<td>Benzene-H$_2$O (C$_s$)</td>
<td>-2.72</td>
<td>-3.28</td>
<td></td>
<td>-4.16</td>
</tr>
<tr>
<td>Benzene dimer (C$_{2v}$)</td>
<td>-2.28</td>
<td>-2.74</td>
<td>-2.03</td>
<td>-2.76</td>
</tr>
<tr>
<td>Benzene dimer (C$_{2h}$)</td>
<td>-2.80</td>
<td>-2.73</td>
<td>-2.00</td>
<td>-2.35</td>
</tr>
<tr>
<td>AT (stack)</td>
<td>-9.55*</td>
<td>-12.23</td>
<td>-10.47</td>
<td>-12.85</td>
</tr>
</tbody>
</table>

*Not optimized


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
From the Nucleic Acid Database\(^\dagger\): [http://ndbserver.rutgers.edu]

- Twist = 36.0 ± 6.8°
- Rise = 3.32 ± 0.19 Å

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

<table>
<thead>
<tr>
<th></th>
<th>Our results</th>
<th>Nucleic acid database</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Pair</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GA:TC</td>
<td>33.7° ± 9.4°</td>
<td>36.0° ± 6.8°</td>
</tr>
<tr>
<td>GT:AC</td>
<td>3.52 ± 0.05 Å</td>
<td>3.32 ± 0.19 Å</td>
</tr>
</tbody>
</table>

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.


*Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, JACS, 130, 1304, (2008)
Thymine Interactions in DNA

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

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

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

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

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Cooper, Thonhauser, Puzder, Schröder, Lundqvist and Langreth, JACS, 130, 1304, (2008)
Sequence-dependent Twist


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

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

Solid state storage materials are the way to go!

Honda FCX Clarity
Metal Hydrides

- Store H$_2$ as dissociated H atoms in a metal lattice

- Advantage
  - relatively high gravimetric densities at ambient T$^\circ$
  - and moderate p

- Disadvantages
  - poor reversibility
  - slow adsorption and desorption rates

- Doping (e.g. with Ti) can enhance kinetics
Carbon based H$_2$ storage

- H$_2$ stored as physisorbed molecules
  - Graphite, buckyballs, carbon nanotubes

- Advantages
  - Excellent reversible H$_2$ storage,
  - Storage density directly linked to available surface area

- Disadvantages
  - High cost
  - Low storage capacity
  - Poor sample reproducibility

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 \([M_2(bdc)_2(ted)]\)
\([M = \text{Co, Cu, Zn}, \ bdc = \text{benzene dicarboxylate, ted = tri-ethyl diamine}]\)
Left: Sideview of column, Right: 3D framework.
Calculations of fragments such as benzene dicarboxylate (right) are commonly used to simulate the interactions of hydrogen with MOFs.

Goal: To use theoretical methods to explore the adsorption of $\text{H}_2$ within MOF materials.

- Examine differences of modeling MOF fragment and entire MOF
- Explore the importance of the metal cation
H$_2$ interactions with linker fragment

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

Exchange Effects

Benzene Dimer

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

Linker potential energy surface

QC PES

vdW-DF PES

fixed separation distance

optimized separation distance

kJ/mol

kJ/mol

Modeling the true MOF (bdc linker)

Advantages of modeling entire MOF:
• Significant difference (~3 kJ/mol) in \( \text{H}_2 \) binding energy relative to fragment,
• New more stable \( \text{H}_2 \) binding sites now accessible!
Predicting H₂ adsorption sites

- Linker plane preferred binding site, \( \Delta E = -10.0 \text{ kJ/mol} \)
- Pillar plane preferred binding site, \( \Delta E = -11.1 \text{ kJ/mol} \)
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 H$_2$ interactions.
Acknowledgements

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


FIG. 1: (Color online) Butterfly (BF) (top), and tight-bridge (TB) (bottom) structures of C6H6 on Si(001)-(2×1). LHS: viewed along [110]. RHS: viewed along [110] dimer rows.