

# Evaluating van der Waals energies from dielectric response functions

Deyu Lu

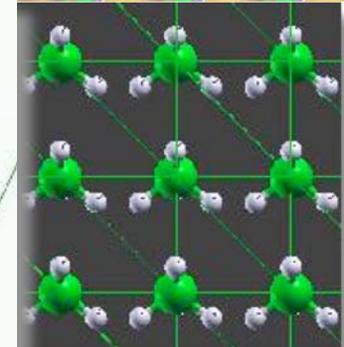
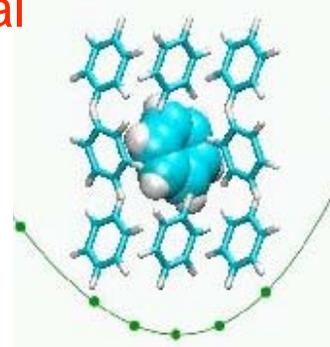
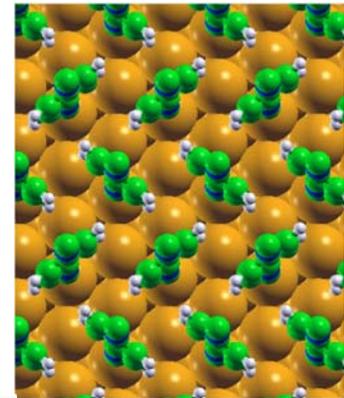
Department of chemistry, UC Davis

Electronic structure workshop, Davis, CA

06/23/2009

# Motivation

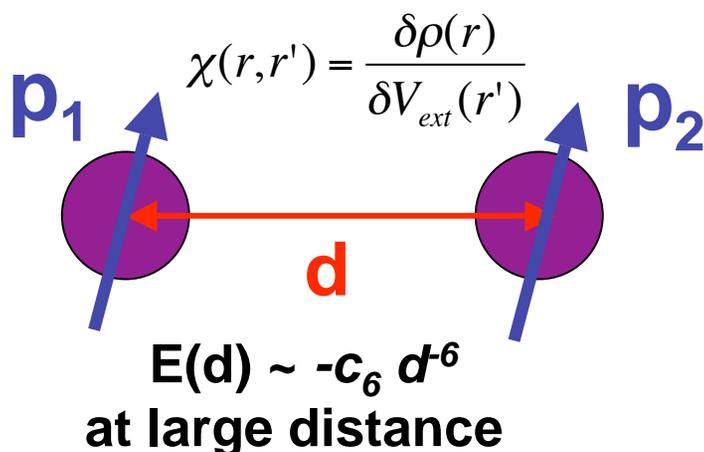
- **vdW forces** play important roles in many processes such as physical absorption, adhesion, assembly of organic molecules, wetting...
- In order to describe the vdW energies accurately, a central ingredient of the theory is the **dielectric response function**, which is **dynamical and non-local** in nature.
- From the practical aspect, evaluation of the dielectric response function from first principles is usually **computationally demanding**. Thus it is important to develop efficient **numerical implementations** suitable for the application to large systems.



# Outline

- Existing vdW methods
- ACFDT theory and numerical implementation
  - RPA correlation energy using dielectric eigenmode expansion technique
  - Examples
    - Benzene crystal
    - Methane phase I
    - PDI SAM on Au(111) surface
- ACFDT with local basis sets
  - Dielectric eigenmodes from linear combination of local basis functions
  - Classification of dielectric eigenmodes of a rare gas atom

# van der Waals interaction



- Standard DFT XC-functionals are short-ranged and fail to describe the very **non-local nature of electron-electron correlation** in vdW systems.
- LDA sometimes provides fortuitous good agreements with experiments; GGA very often fails to bind vdW systems.

## Empirical methods

- Adding  $c_6$  pairwise potential gives qualitative improvement, but it assumes additivity and has issues with transferability.

## Functional based methods

- vdW functional
- Range-separated KS

## General theories

- Quantum chemistry methods (**CCSD, MP2, SAPT, etc**) are very expensive and not feasible for large systems and extended systems.
- QMC (**Poster by Leonardo Spanu**)
- Adiabatic connection fluctuation-dissipation theorem (**ACFDT**), which contains EXX and correlation energy formulated on density-density response function

# RPA correlation energy through ACFDT

**ACFDT:**  $E_{xc} = E_{xx} + E_c$

D. C. Langreth and J.P. Perdew, *Sol. State Commun.*, 17:1425, 1975.

D. C. Langreth and J.P. Perdew, *Phys. Rev. B*, 15:2884, 1977.

$$E_c = -\frac{1}{2\pi} \int_0^1 d\lambda \int dr \int dr' \frac{1}{|r-r'|} \int_0^\infty du \left( \chi^\lambda(r, r', iu) - \chi_{KS}(r, r', iu) \right)$$

$$\chi^\lambda(1,2) - \chi_{KS}(1,2) = \chi_{KS}(1,3) f_{Hxc}^\lambda(34) \chi^\lambda(42)$$

Under RPA:  $\chi^\lambda = \frac{\chi_{KS}}{1 - \lambda \chi_{KS} v_H}$

$$\chi_{KS G, G'}(q, iu) = \frac{2}{\Omega} \sum_k \sum_{n, m} (f_n - f_m) \frac{\rho_{k, q}(G) \rho_{k, q}^*(G')}{iu + \varepsilon_n(k) - \varepsilon_m(k+q)}$$

$$\rho_{k, q}(G) = \langle k, n | e^{-i(\mathbf{q}+\mathbf{G}) \cdot \mathbf{r}} | k+q, m \rangle$$

**Short range correction:**

$$E_c^{RPA+} = E_c^{RPA} + \left( E_c^{LDA/GGA} - E_c^{RPAmodel} \right)$$

# Features of the EXX/RPA approach

- It is **self-interaction free** due to the use of exact exchange.
- **RPA correlation** (ACFDT) treats long-range correlation accurately
- **Short-range correction** of correlation (RPA+)  
RPA+ usually does not significantly affect the binding curve and cohesive energy due to error cancellation
- Because exchange and correlation are calculated **separately**, they both need to be converged very well, in contrast to LDA or GGA xc energies, which have huge error cancellation.
- The standard implementation is computationally quite demanding, which scales as  $N_v N_{pw}^3$ .
- We apply density functional perturbation theory to improve the scaling to  $N_v^2 N_{eig} N_{pw}$ , which makes it possible for the calculation of large systems.

D. Lu, Y. Li, D. Rocca and G. Galli, *Phys. Rev. Lett.*, 102, 206411, 2009.

Y. Li, D. Lu, and G. Galli, *in preparation*.

# Existing Works

## Jellium

- J. F. Dobson and J. Wang, *Phys. Rev. Lett.*, 82, 2123 (1999);  
J. F. Dobson and J. Wang, *Phys. Rev. B*, 62, 10038 (2000);  
J. M. Pitarke and J. P. Perdew, *Phys. Rev. B*, 67, 045101 (2003);  
J. Jung, P. Garca-Gonzalez, J. F. Dobson, and R. W. Godby, *Phys. Rev. B*, 70, 205107 (2004).

## Isolated molecule

- M. Fuchs and X. Gonze, *Phys. Rev. B*, 65, 235109 (2002); (H<sub>2</sub>, Be<sub>2</sub>)  
F. Aryasetiawan, T. Miyake, and K. Terakura, *Phys. Rev. Lett.*, 88, 166401 (2002); (H<sub>2</sub>)  
F. Furche and T. V. Voorhis, *J. Chem. Phys.* 122, 164106 (2005); (He<sub>2</sub> and HeNe)  
J. Toulouse, I. C. Gerber, G. Jansen, A. Savin, and J. G. Angyan, *Phys. Rev. Lett.*, 102, 096404 (2009); (Be<sub>2</sub> and Ne<sub>2</sub>)  
H.-V. Nguyen and S. de Gironcoli, *Phys. Rev. B*, 79, 205114 (2009) (Be<sub>2</sub>)

## Compact solid

- T. Miyake et al., *Phys. Rev. B* 66, 245103 (2002). (Na, Si)  
P. Garcia-Gonzalez, J. Fernandez, A. Marini, and A. Rubio, *J. Phys. Chem. A*, 111, 12458 (2007).  
(Si, NaCl, Jellium Clusters)

## Layered material

A. Marini, P. Garcia-Gonzalez, and A. Rubio, *Phys. Rev. Lett.* 96, 136404 (2006). **[h-BN layers]**

## Noble gas solid

J. Harl and G. Kresse, *Phys. Rev. B* 77, 045136 (2008). **[fcc Ne, Ar, and Kr crystal]**

## Physisorption on metal surface

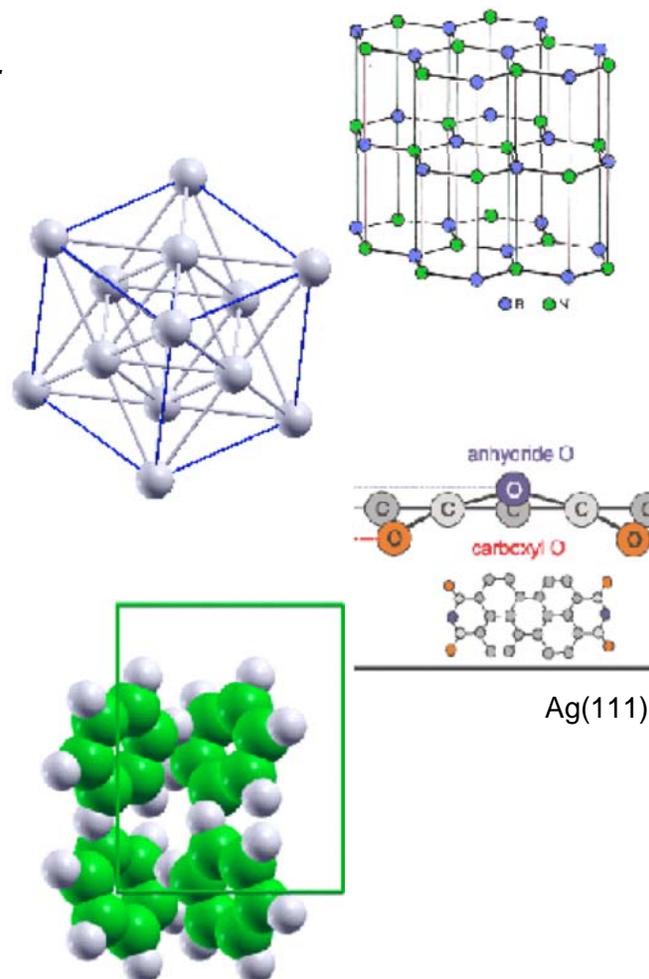
M. Rohling and T. Bredow, *Phys. Rev. Lett.* 101, 266106 (2008). **[Xe, PTCDA on Ag(111)]**

## vdW Crystal

D. Lu, Y. Li, D. Rocca and G. Galli, *Phys. Rev. Lett.* 102, 206411, (2009). **[Benzene crystal]**

## Formulation based on excitation energies

F. Furche, *J. Chem. Phys.* 129, 114105, (2008). **[theory]**



remove the  $\lambda$   
integration

## Eigenmode expansion of $E_c^{\text{RPA}}$

$$\begin{aligned}v^{1/2}(q) &= \sqrt{4\pi}/q \\ \tilde{\epsilon} &= 1 - v^{1/2} \chi_{KS} v^{1/2} \\ &= \sum_i |i\rangle \epsilon_i \langle i|\end{aligned}$$

$$\begin{aligned}-\int_0^1 d\lambda v^{1/2} \chi^\lambda v^{1/2} &= \text{Log}(I - v^{1/2} \chi_{KS} v^{1/2}) \\ &= \sum_i |i\rangle \text{Log}(\epsilon_i) \langle i|\end{aligned}$$

Need to  
compute  $\epsilon_i$  !

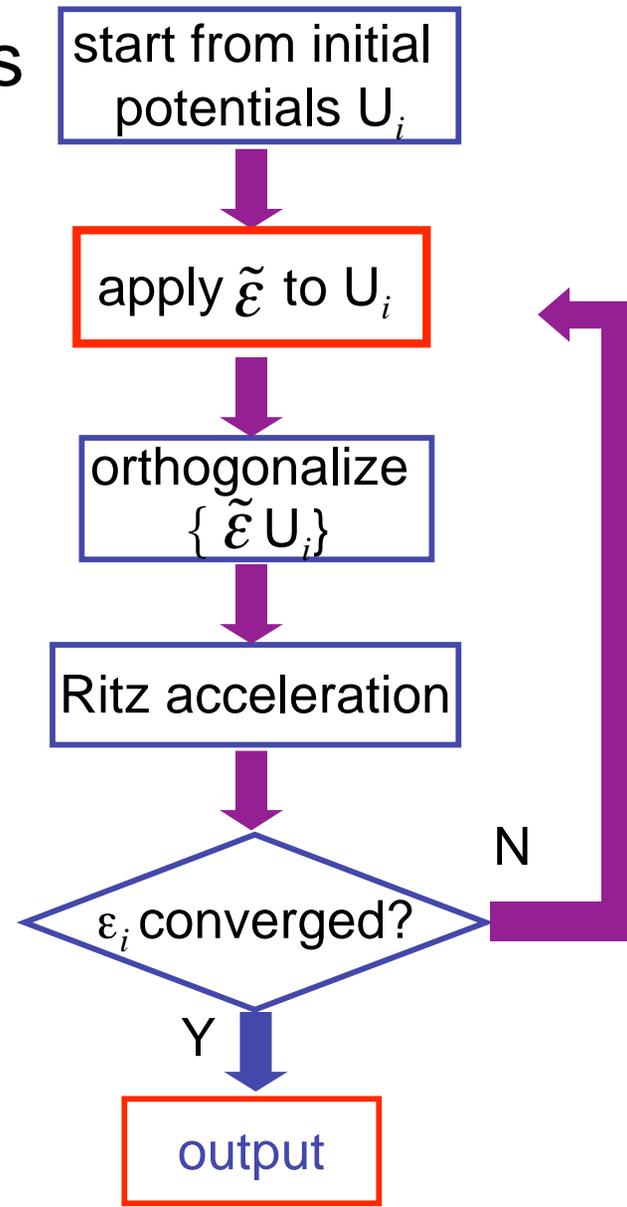
$$E_c = \frac{1}{2\pi N_q} \int_0^\infty du \sum_q \sum_i \{ \text{Log}[\epsilon_i(q, iu)] - \epsilon_i(q, iu) + 1 \}$$

# Solving the dielectric eigenmodes with an iterative method

- Eigenpotentials are found by repeated application of the operator  $\tilde{\epsilon}$
- Effect of XC kernel (not in RPA) in the perturbation can be easily included
- Implemented through a modified version of the phonon code in the Quantum Espresso package\*

H. Wilson, F. Gygi and G. Galli, *Phys. Rev. B*, 78:113303, 2008.  
H. Wilson, D. Lu, F. Gygi and G. Galli, *Phys. Rev. B*, 79, 245106, 2009.  
V. Nguyen and S. de Gironcoli, *Phys. Rev. B*, 79, 205114, 2009.

\* P. Giannozzi et al., <http://www.quantum-espresso.org>

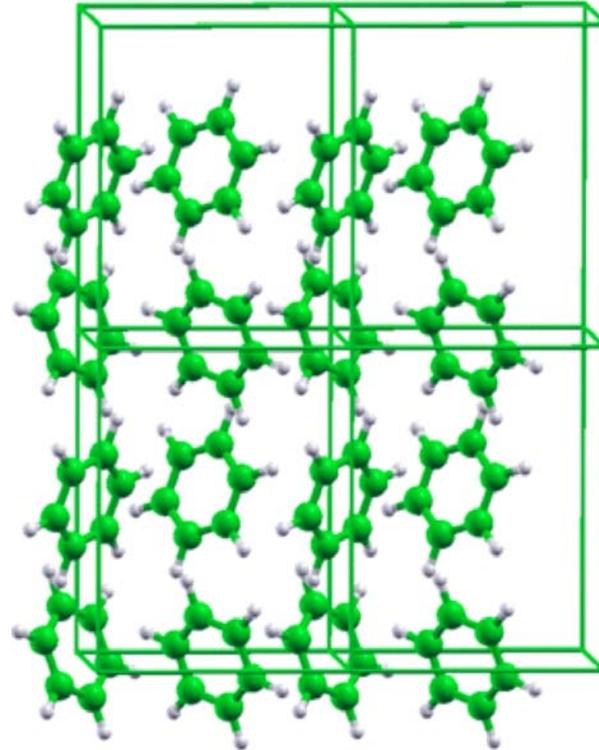


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# Benzene Crystal

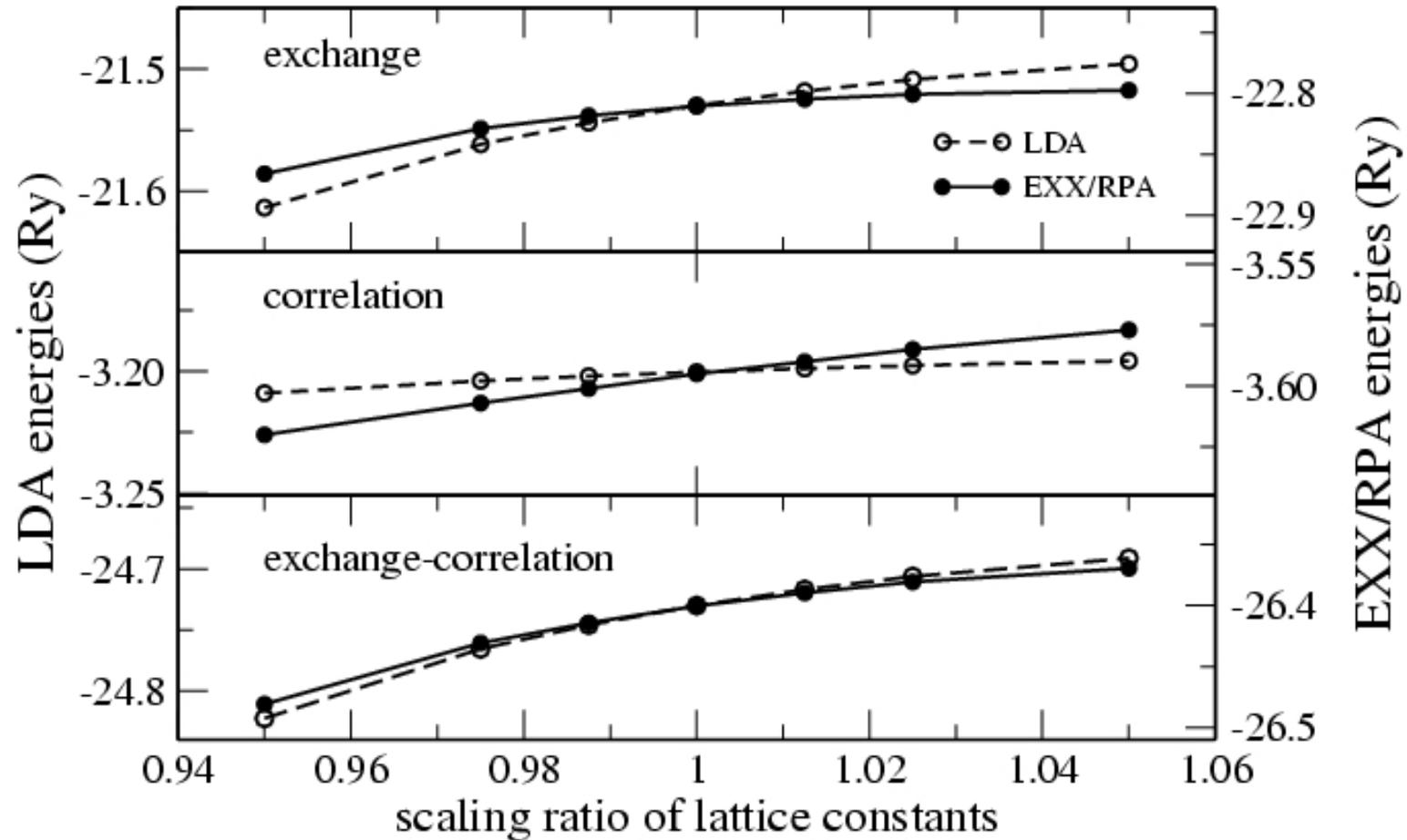
- One of the simplest organic crystals bound by vdW forces
- Experimental lattice constants (4K) [1]:
  - Four monomers per cell
  - Pbc<sub>a</sub> symmetry
  - $a=7.360 \text{ \AA}$ ,  $b=9.375 \text{ \AA}$ ,  
 $c=6.70 \text{ \AA}$ ,  $\alpha=\beta=\gamma=90^\circ$
- LDA overestimates the equilibrium density by **13%**; PBE underestimates the equilibrium density by **27%** and severely under-binds<sup>[2]</sup>.



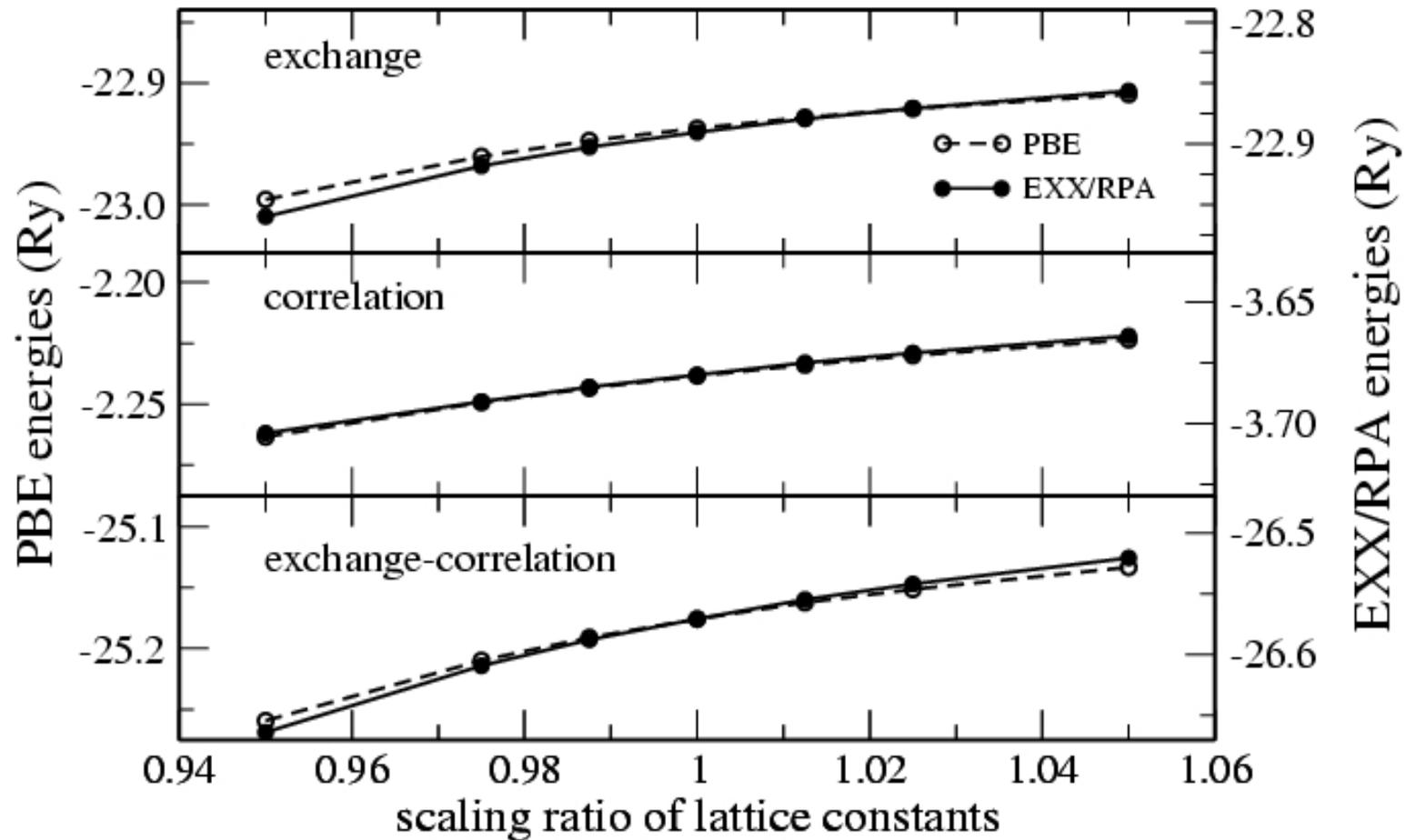
[1] W. David, R. Ibberson, G. Jeroy, and J. Ruble, *Physica B*, 180-181, 597, 1992.

[2] D. Lu, Y. Li, D. Rocca and G. Galli, *Phys. Rev. Lett.*, 102, 206411, 2009.

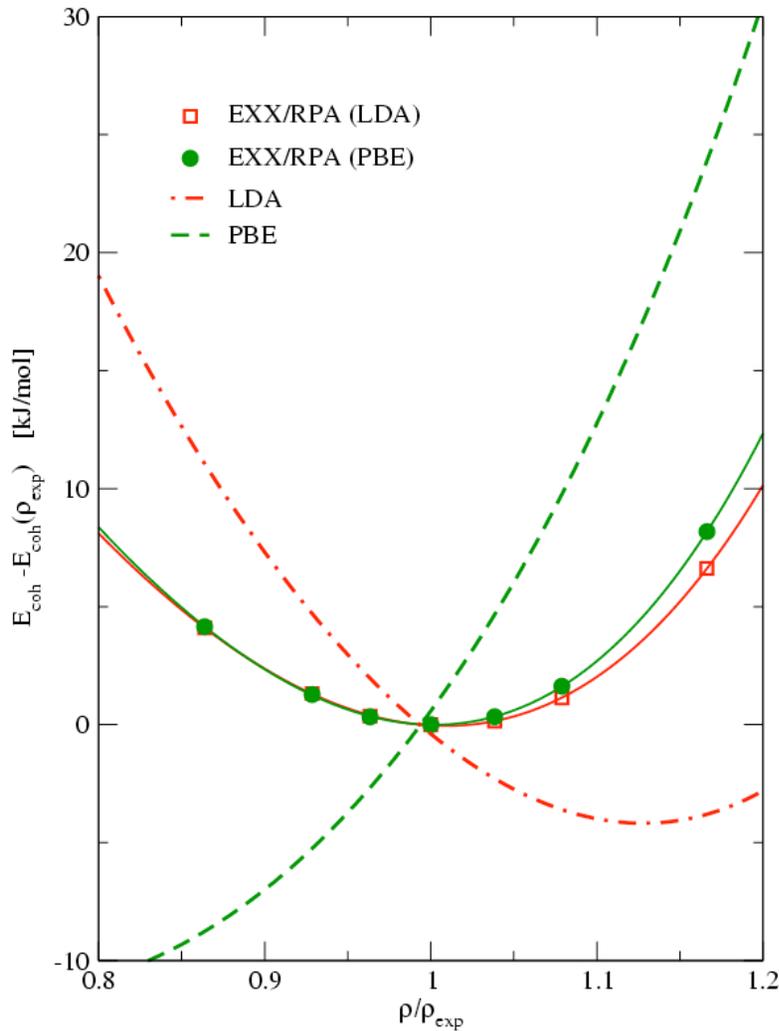
# EXX/RPA from LDA ground states



# EXX/RPA from PBE ground states



# Binding curve



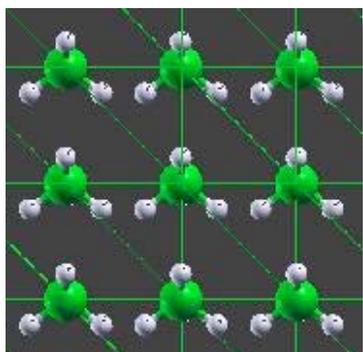
	LDA	EXX/RPA (LDA)	PBE	EXX/RPA (PBE)	Exp.
$\rho_0 / \rho_{\text{exp}}$	1.13	1.01	0.73	1.00	1.00
$E_{\text{coh}}$ [kJ/mol]	56	44	11	47	50-54
$B_0$ [GPa]	10	7	2	7	$\sim 8$

Exp.: (1) W. David, R. Ibberson, G. Jeffrey, and J. Ruble, *Physica B*, 180-181: 597, 1992; (2) J. Chickos and W. Acree, Jr., *J. Phys. Chem. Ref. Data*, 31:537, 2002.

- EXX/RPA predicts equilibrium density, cohesive energy, and bulk modulus in good agreement with experiment.
- The binding curve is **insensitive** to the exchange-correlation functional in the ground state calculation.
- Short-range correction (**EXX/RPA+**) does not change the binding curve but reduces the cohesive energy by about **2 kJ/mol**.
- Semi-empirical DFT+D (**pair-potential correction**), e.g., Grimme06 parameterization, yields excellent cohesive energy but the equilibrium density is about **10%** too large.

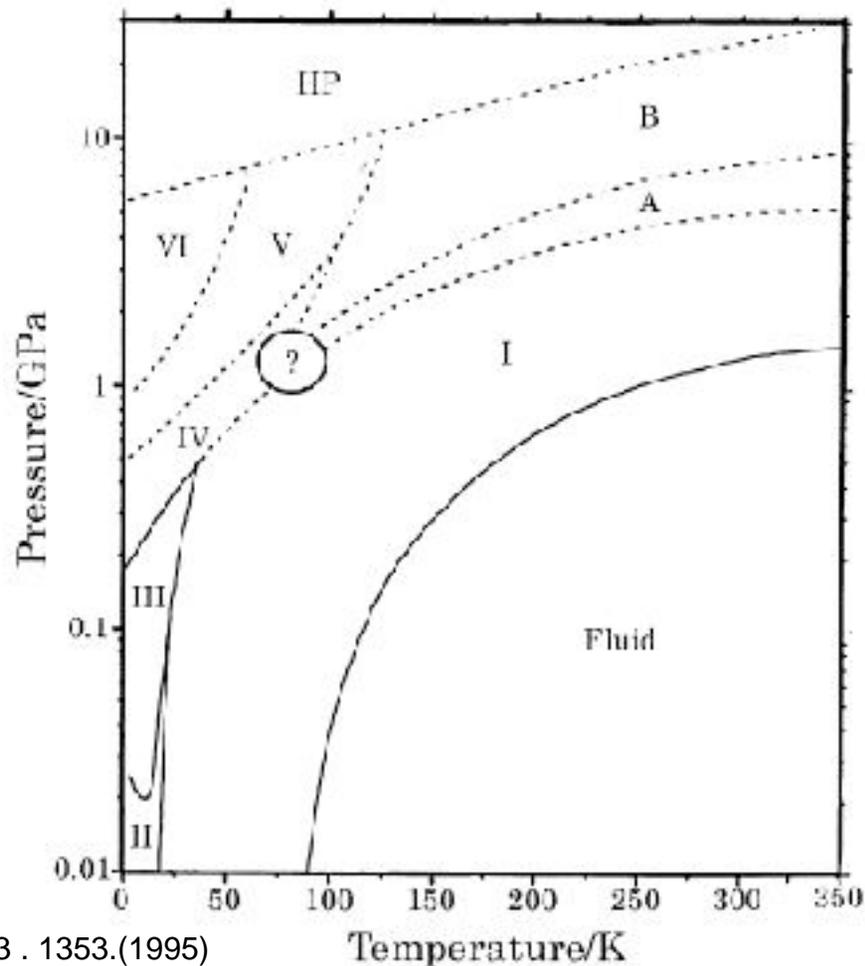
D. Lu, Y. Li, D. Rocca and G. Galli, *Phys. Rev. Lett.*, 102, 206411, 2009.

# Methane crystal



- Phase I: fcc structure, with one **freely** rotating molecule in the unit cell.
- Existing theoretical work ignored rotational degree of freedom [3-4]

phase diagram of methane<sup>[1,2]</sup>



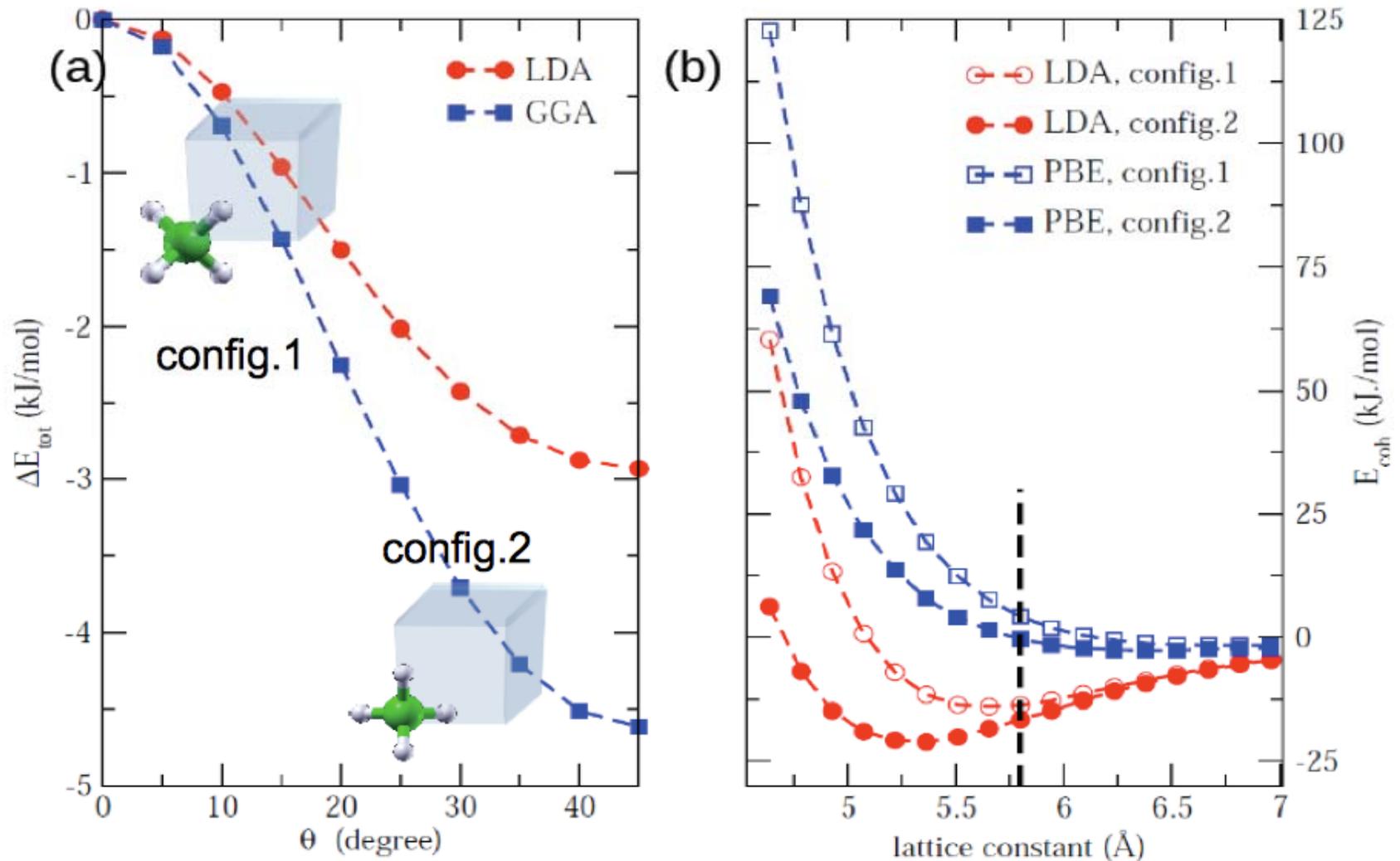
[1] R. Bini, G. Pratesi, *Phys. Rev. B* 55 14800 (1997).

[2] R. Bini, L. Ulivi, H.J. Jodi, P.R. Salvi, *J. Chem. Phys.* 103 . 1353.(1995)

[3] B. Kunz, *Phys.: Condens. Matter* 6 L233-LZ37.(1994)

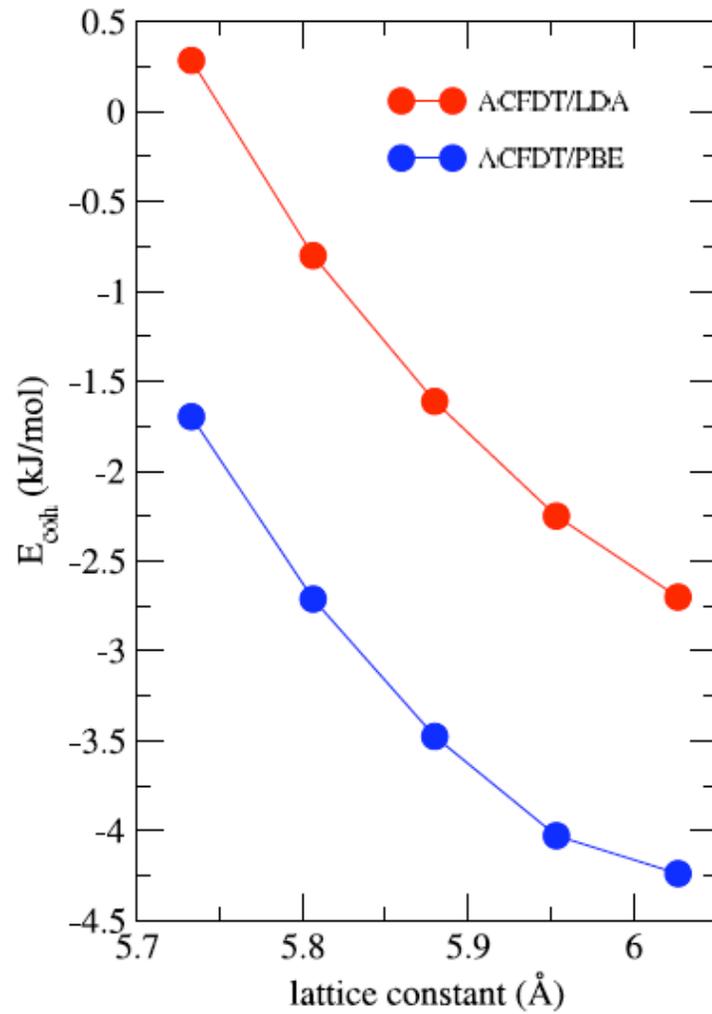
[4] T.Kerber, M. Sierka and J. Sauer, *J. Compt. Chem*, 29, 2088 (2008)

# Is the orientation important?

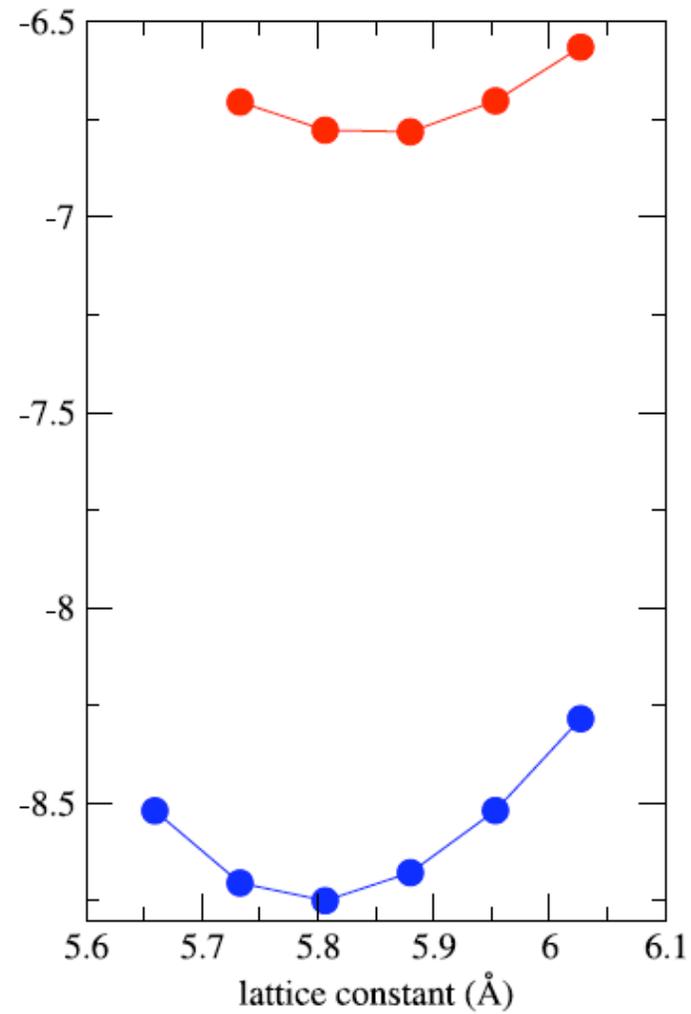


# EXX/RPA binding curve

config.1



config. 2



# EXX/RPA (PBE) results

config.	EXX/RPA	PBE+D <sup>a</sup>	PBE+D <sup>b</sup>	MP2 <sup>c</sup>	exp.
1 $a_0$	>6	5.84	5.80	6.00	plastic phase
1 $E_{\text{coh}}$	–	10.8	11.35	10.3	
2 $a_0$	5.80	5.50	–	–	$a_0 \sim 5.84^d$
2 $E_{\text{coh}}$	8.8	14.9	–	–	$E_{\text{coh}} = 10.4\text{--}11.4^e$

a: This work from PBE ground state. Dispersion corrections were evaluated with Grimme2006 parametrization scheme. [S. Grimme, *J. Comp. Chem.* 27, 1787 (2006)].

b: T. Kerber, M. Sierka, and J. Sauer, *J. Comput. Chem.* 29, 2088 (2008).

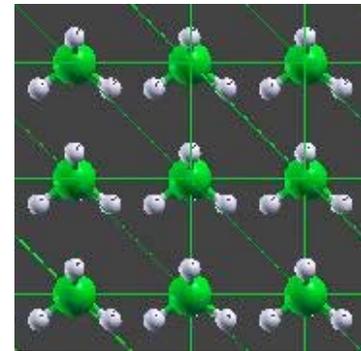
c: A. B. Kunz, *J. Phys. : Condens. Matter.* 6, L233 (1994)

d:  $a_0 = 5.84 \text{ \AA}$  was measured at 29K.

e: The measured heat of sublimation (in kJ/mol) is corrected for temperature effects ZPE is not included.

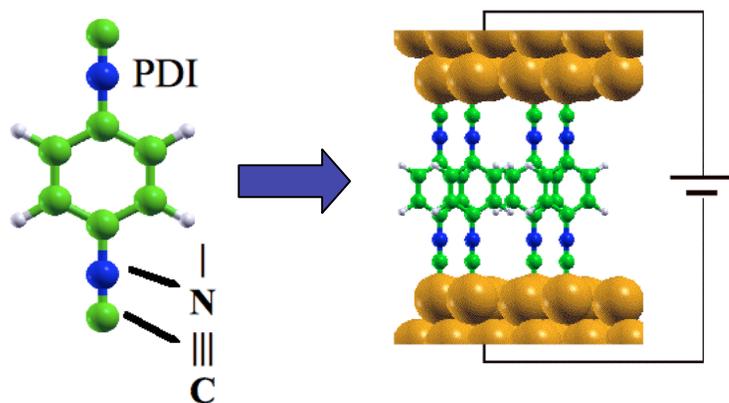
# Summary on methane crystal

- **Orientations** of methane molecules in the *fcc* structure were found to **contribute significantly to the intermolecular interaction energy**, both at the DFT level and the EXX/RPA level.
- The cohesive energy from EXX/RPA (LDA) is about **2 kJ/mol** smaller than EXX/RPA (PBE).
- Comparing to EXX/RPA, semi-empirical **DFT+D** method **underestimates the lattice constant** and **overestimates the cohesive energy**.
- Quantum effects may need to be incorporated to recover experimentally observed plastic phase (random orientations).

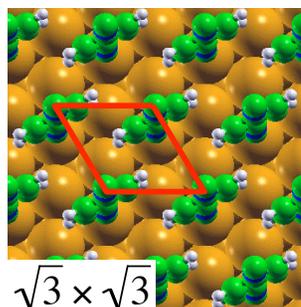


Y. Li, D. Lu, and G. Galli, *in preparation*.

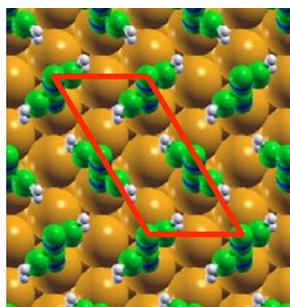
# PDI SAM on Au(111) surface: Is Isocyanide group a good linker?



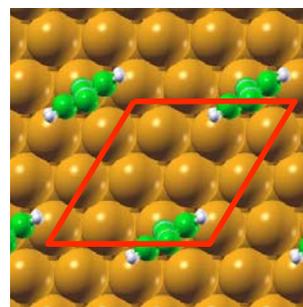
- The presence of the triple bond in the isocyanide group may effectively connect the  $p\pi$  electrons in the aromatic moiety and the  $d\pi$  electrons on the gold surface.
- However, no ordered monolayers of PDI or BPDI has been observed in either AFM or STM experiments.
- DFT (LDA or GGA) does not describe well vdW interactions among SAMs.



full coverage:  
1 PDI / 3 Au



full coverage:  
Herringbone



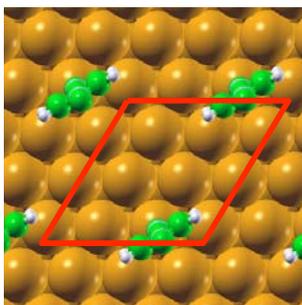
low coverage (1/3):  
1 PDI / 9 Au

Which one is more stable?

# DFT(PBE) results for PDI/Au(111)

$$E_{ad} = -(E_{\text{mol/Au}} - E_{\text{Au}} - E_{\text{mol}}) = E_{\text{mol-Au}} + E_{\text{mol-mol}}$$

coverage	$E_{\text{mol-Au}}$ (eV)	$E_{\text{mol-mol}}$ (eV)	$E_{ad}$ (eV)
PDI/Au(111), atop			
1 ( $\sqrt{3} \times \sqrt{3}$ )	0.44	-0.38	0.06
1 ( <i>Herringbone</i> )	0.46	-0.22	0.24
1/3	0.59	-0.05	0.54



1. Is PDI intermolecular interaction indeed repulsive?
2. Is the low coverage structure more stable?

Y. Li, D. Lu, S. Swanson, J. C. Scott and G. Galli, *J. Phys. Chem. C* 112, 6413 (2008)  
 Y. Li, D. Lu, and G. Galli, *in preparation*.

# RPA vdW energy in PDI SAM

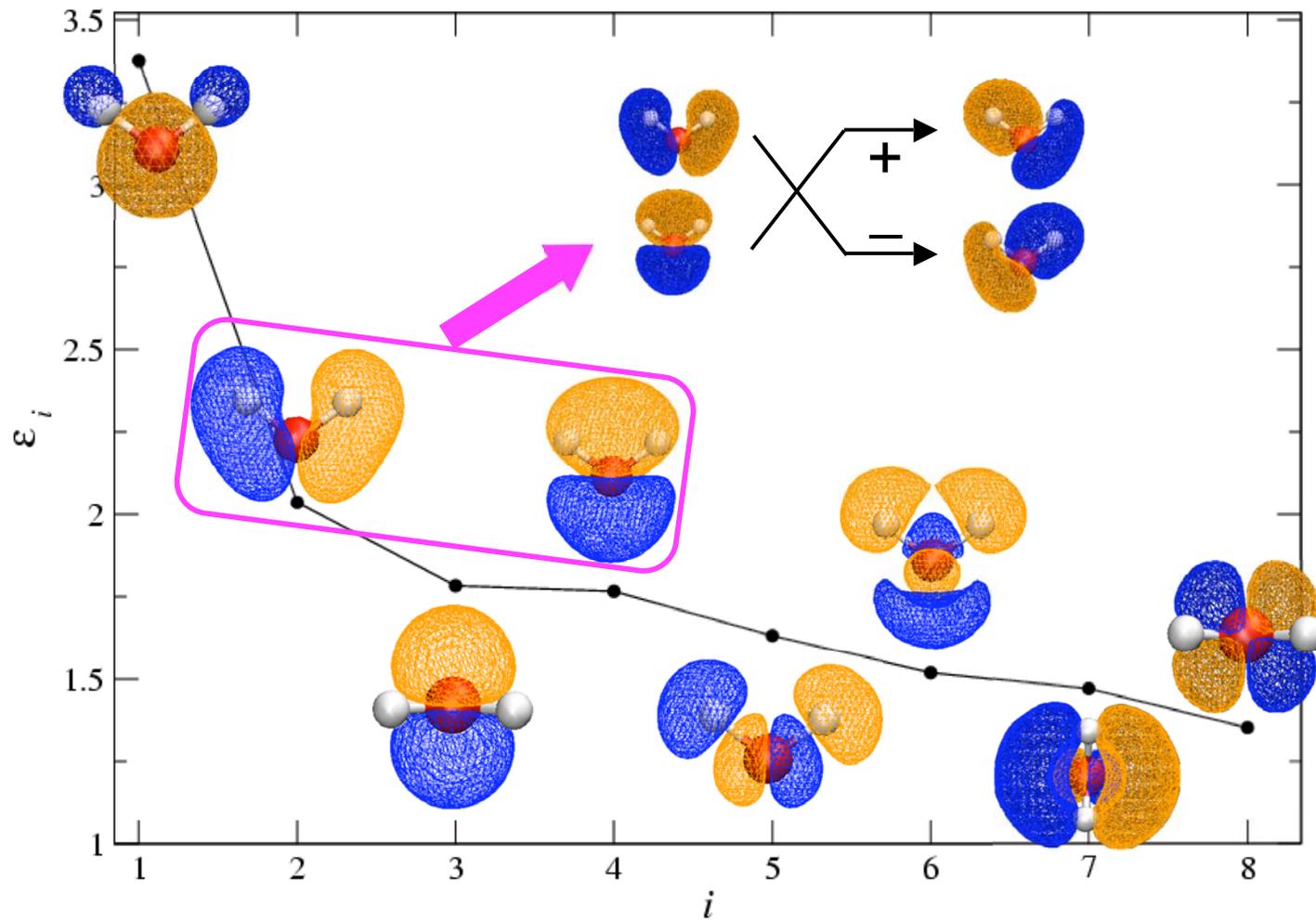
	$E_{\text{mol-mol}}$			$E_{\text{Au-mol}}$ PBE
	PBE	EXX/RPA	PBE+D	
$(\sqrt{3} \times \sqrt{3})$	-0.38	-0.01	-0.002	0.44
<i>herringbone</i>	-0.22	0.15	0.11	0.46
gas phase	0	-	-	0.60

- EXX/RPA greatly improves the under-binding in PBE for PDI SAMs at high packing density.
- Contrary to the case of methane, PBE+D agrees reasonably well with EXX/RPA.
- The adsorption energy of the gas phase and the high coverage herringbone structure are nearly identical.
- The lack of ordering in experiments may arise from the close competition between vdW interactions at high density and stronger surface binding at low density.

# Outline

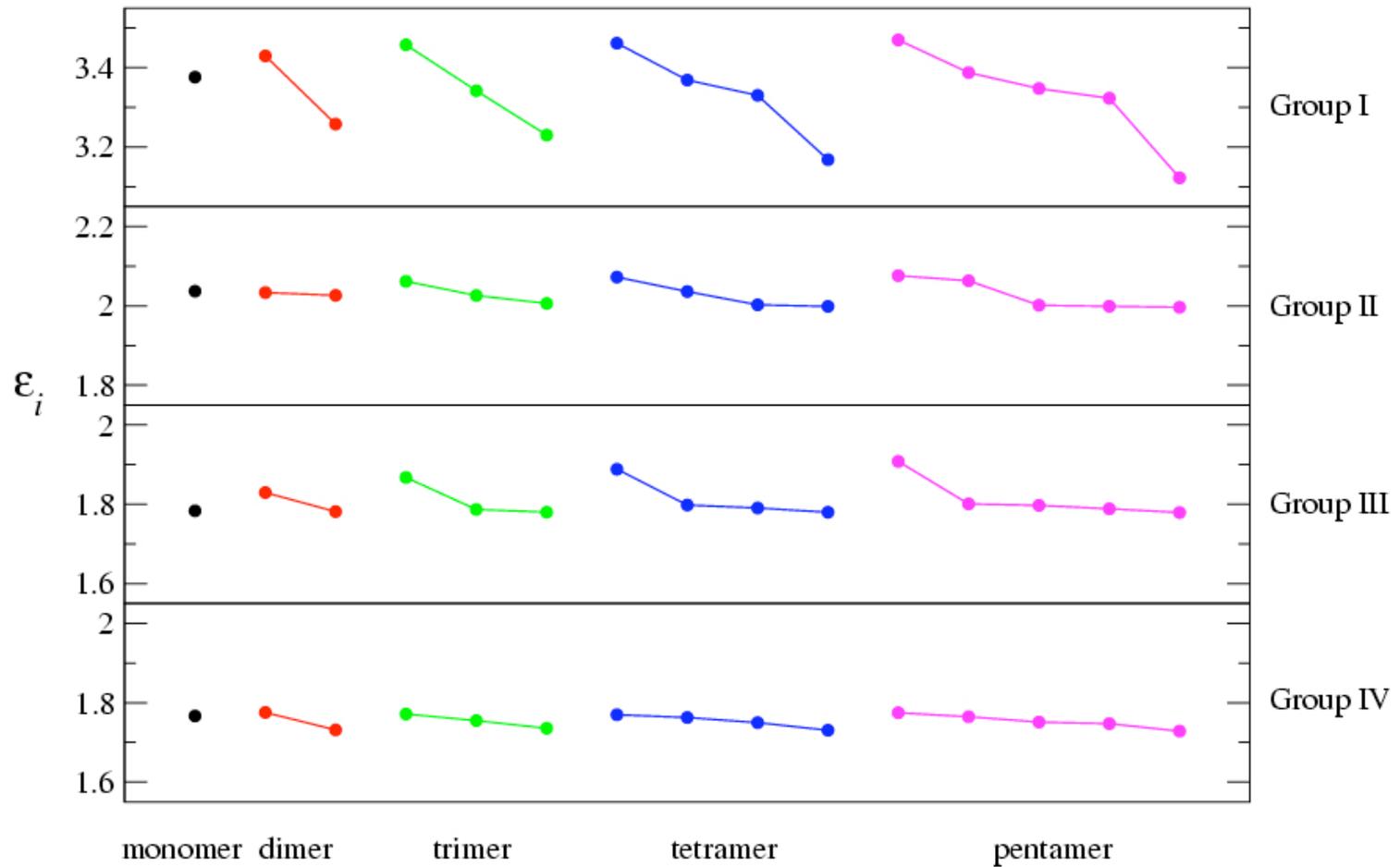
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# DEMs of gas phase water monomer

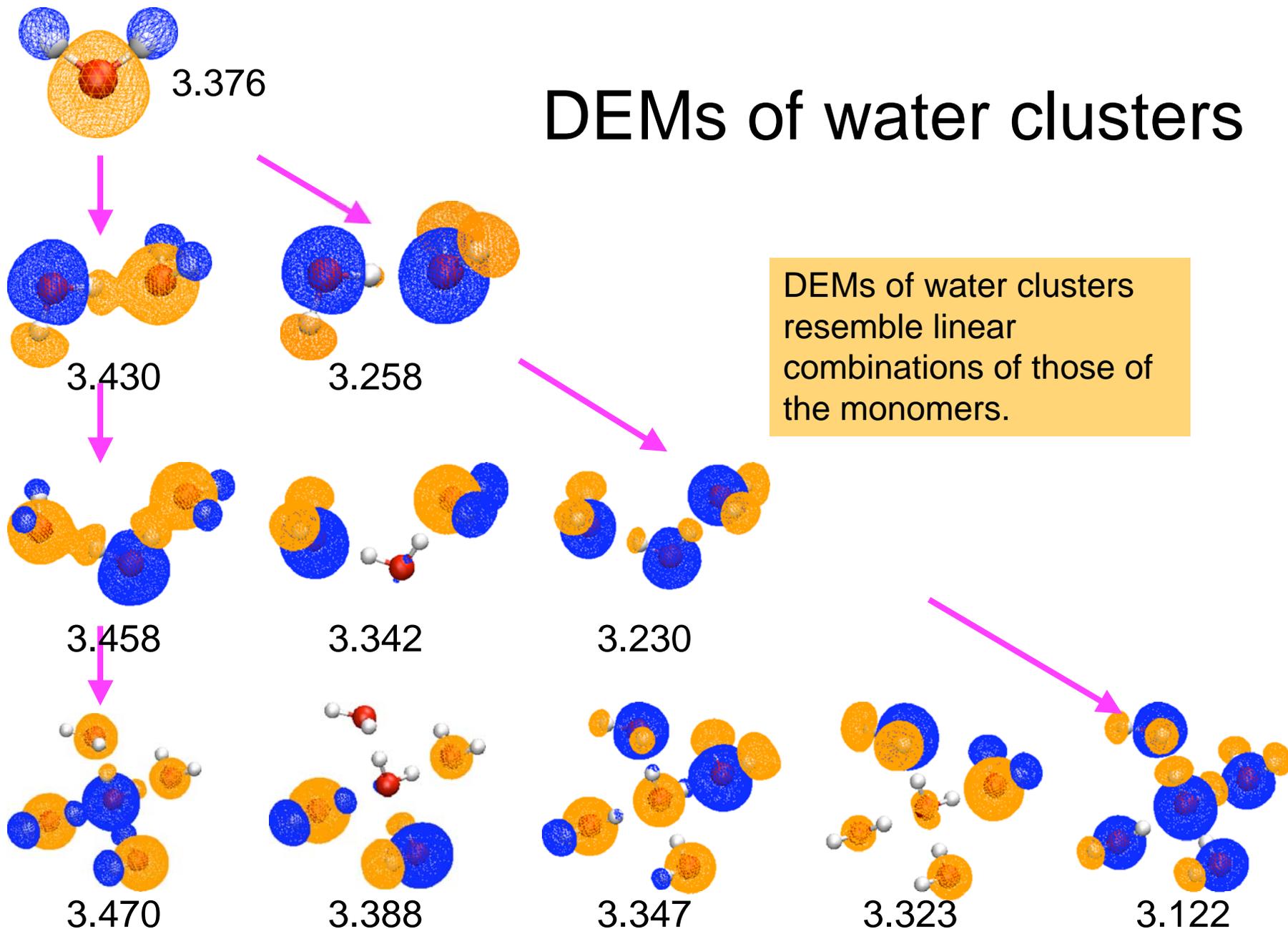


D. Lu, F. Gygi, and G. Galli, *Phys. Rev. Lett.*, 100:147601, 2008.

# DEMs of water clusters



# DEMs of water clusters



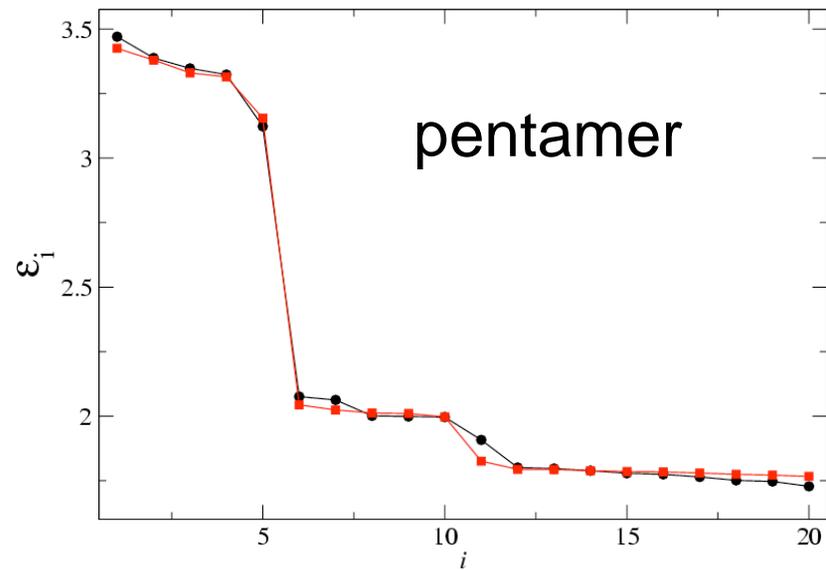
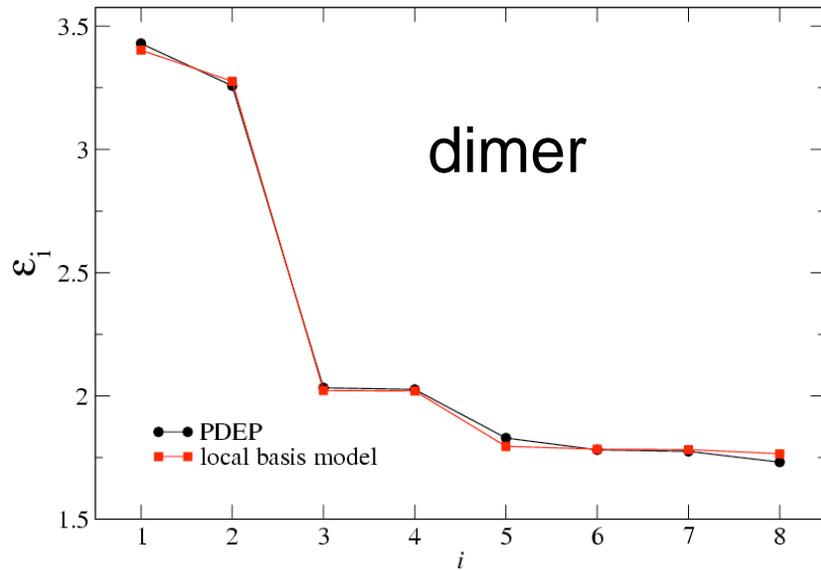
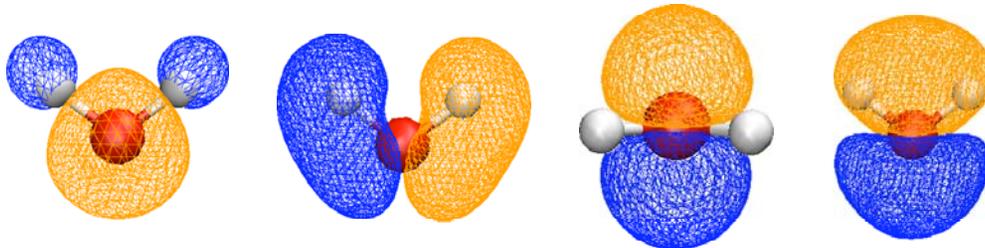
# DEMs from local basis functions

- Represent DEMs in groups I - IV of water clusters by linear combination of local basis functions derived from dielectric response of a monomer
- Compute the elements of **coupling matrix and overlap matrix** for **only once**
- Solving the eigenvalues of  $\epsilon$  from the secular equation:

$$\langle U_i | \tilde{\epsilon} | U_j \rangle - \lambda \langle U_i | U_j \rangle = 0$$

# DEMs from local basis functions

Linear combination of:



# Summary

- We have developed a new implementation of EXX/RPA with the scaling of  $N_v^2 N_{eig} N_{pw}$ , which allows the theory to be applied to reasonably large systems.
- The feasibility of the implementation is demonstrated by applications to a variety of systems with different geometries and bonding properties.
- Good agreement has been found between the ACFDT and experimental results, with EXX/RPA (PBE) yielding slightly better results.
- We found that the empirical method gives qualitative improvement over LDA(GGA), but the quantitative results need to be taken with caution.

H. Wilson, F. Gygi and G. Galli, *Phys. Rev. B*, 78:113303, 2008.

H. Wilson, D. Lu, F. Gygi and G. Galli, *Phys. Rev. B*, 79, 245106, 2009.

D. Lu, Y. Li, D. Rocca and G. Galli, *Phys. Rev. Lett.*, 102, 206411, 2009.

Y. Li, D. Lu, and G. Galli, *in preparation*.

# Work in progress

- The computational cost of ACFDT may be further reduced by considering the dielectric eigenpotentials as the **linear combination of the local response basis functions**, analogous to the tight-binding type of models.
- Preliminary study on water clusters shows very promising results.
- Application and validation of the local basis approach for rare gas dimers may provide further insight of vdW theory from a microscopic point of view.

# Acknowledgement

## Collaborators

- Dr. Yan Li
- Dr. Hugh Wilson
- Dr. Dario Rocca
- Dr. Huy-Viet Nguyen
  
- Prof. François Gygi
- Prof. Giulia Galli
  
- the Angstrom group



# See also related posters

1. van der Waals interactions in weakly-bonded molecular systems from first principles: *An adiabatic-connection fluctuation-dissipation theorem* approach
2. Optical properties of nanostructures from novel density matrix based methods
3. The nature and strength of inter-layer binding in graphene