Van der Waals

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Current: Argonne Leadership Computing Facility
Future: Chemistry Department, Basel University

Overview

- Tutorial (first half)
  - Why do we care?
  - What is it?
  - What's the problem with vdW?
- Recent contributions (second half)
  - Many-body dispersion in DFT
  - 3-body dispersion effects
  - Many-body dispersion effects

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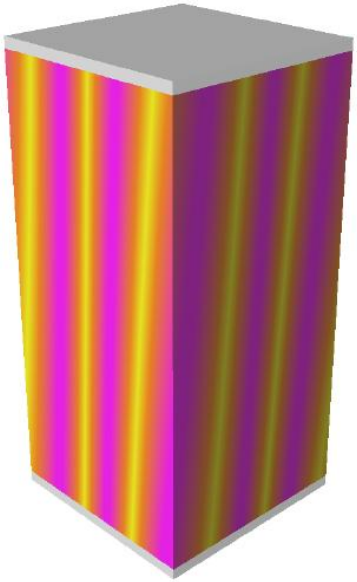
Why do we care?

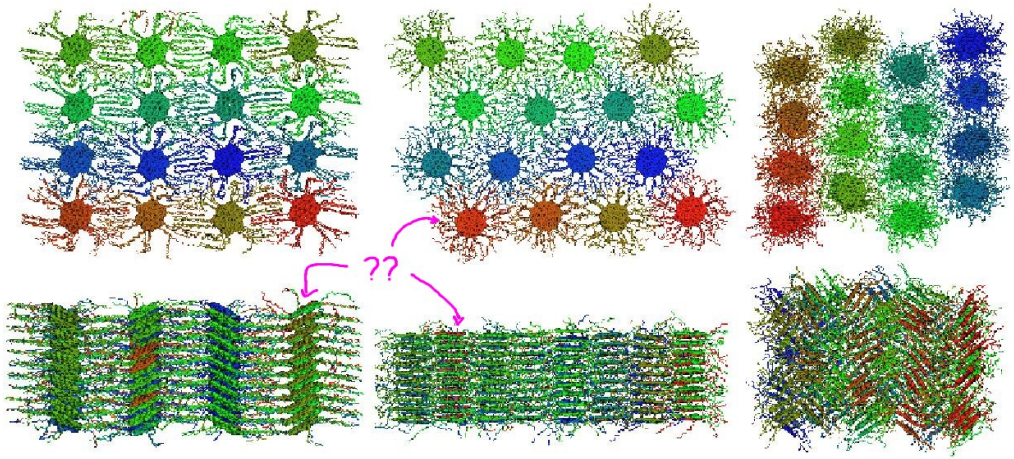
- ``There is plenty of room at the bottom'' (Feynman)
- Intermolecular bonds are weaker than chemical bond, yet crucial for many highly relevant processes
  - Self-assembly
  - Supra-molecular
  - Adhesion, adsorption, physisorption
  - Liquid phase (Solid covalent, Gas ideal)
  - Nano- and meso-scale objects
  - Soft matter
  - Biological systems

Why do we care?



$$k = \frac{J^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}}\exp\left[-\frac{\lambda}{4k_B T}\right]$$

Papers by D. Andrienko et al,
OAvL & Andrienko, JCP (2007)

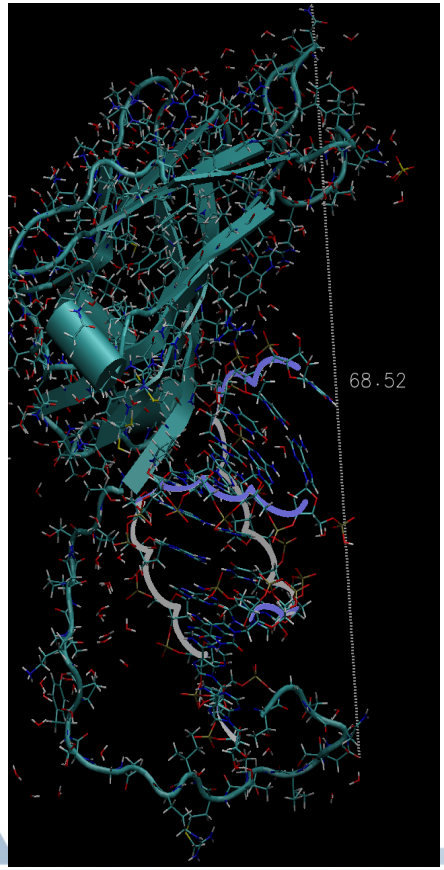


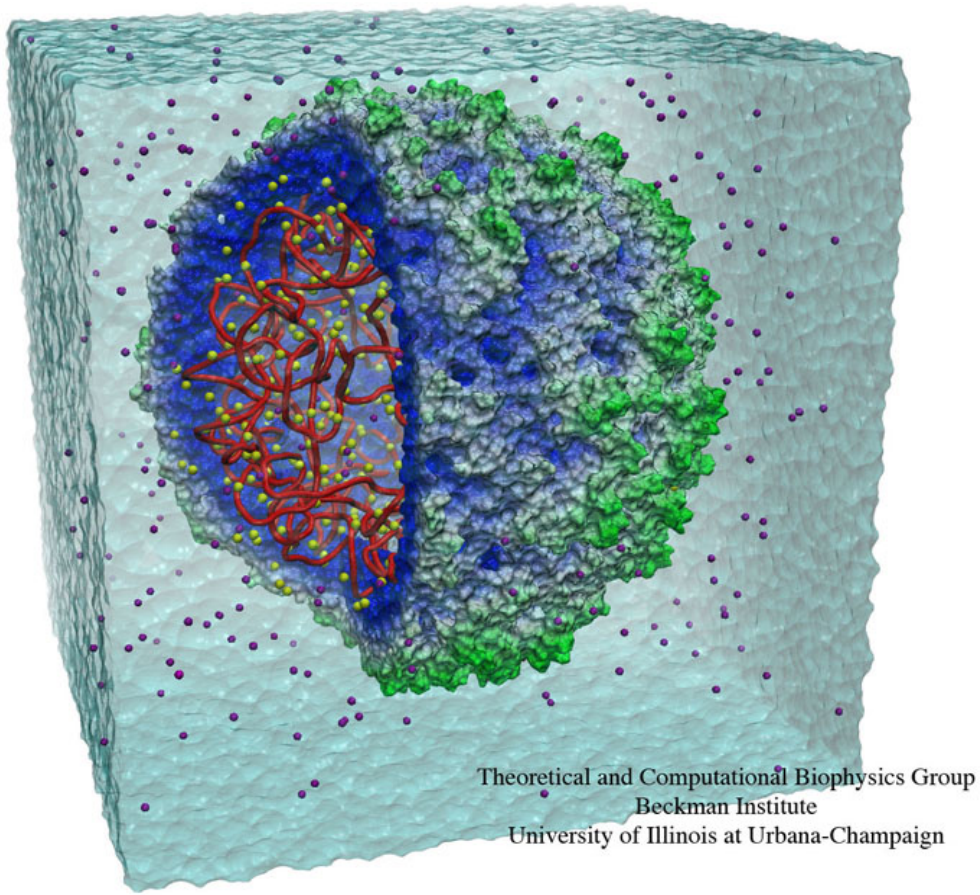
Herringbone (300 K) and hexagonal (400 K) configurations of C_{12}; columnar disordered (400 K) of C_{10-6}

Why do we care?

Molecular dynamics of satellite tobacco mosaic virus (STMV), complete with protein, RNA, ions, and water

K. Schulten and coworkers (2006-)





Icosahedral structure with 3 units/face
→ 3k atom x 3 x 20 ~ 180k atom ~ 1m atom in solution
for tens of nanoseconds
→ Coarse-graining to 5k particle for microseconds

Parallelization across atoms → Natoms < Ncores

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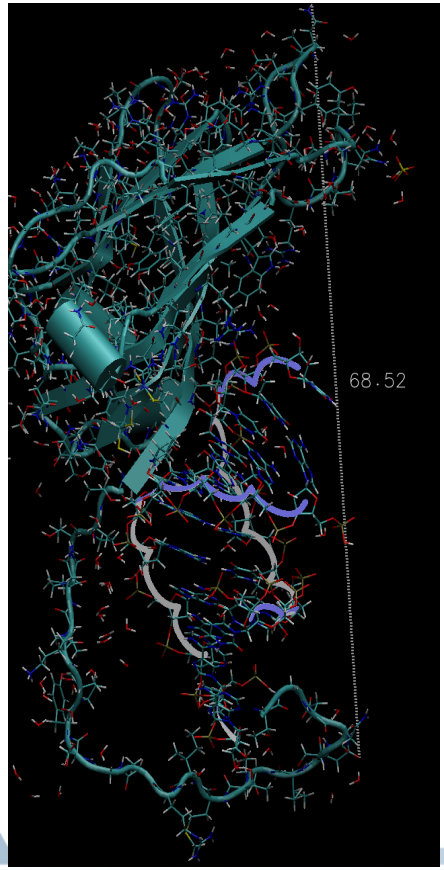

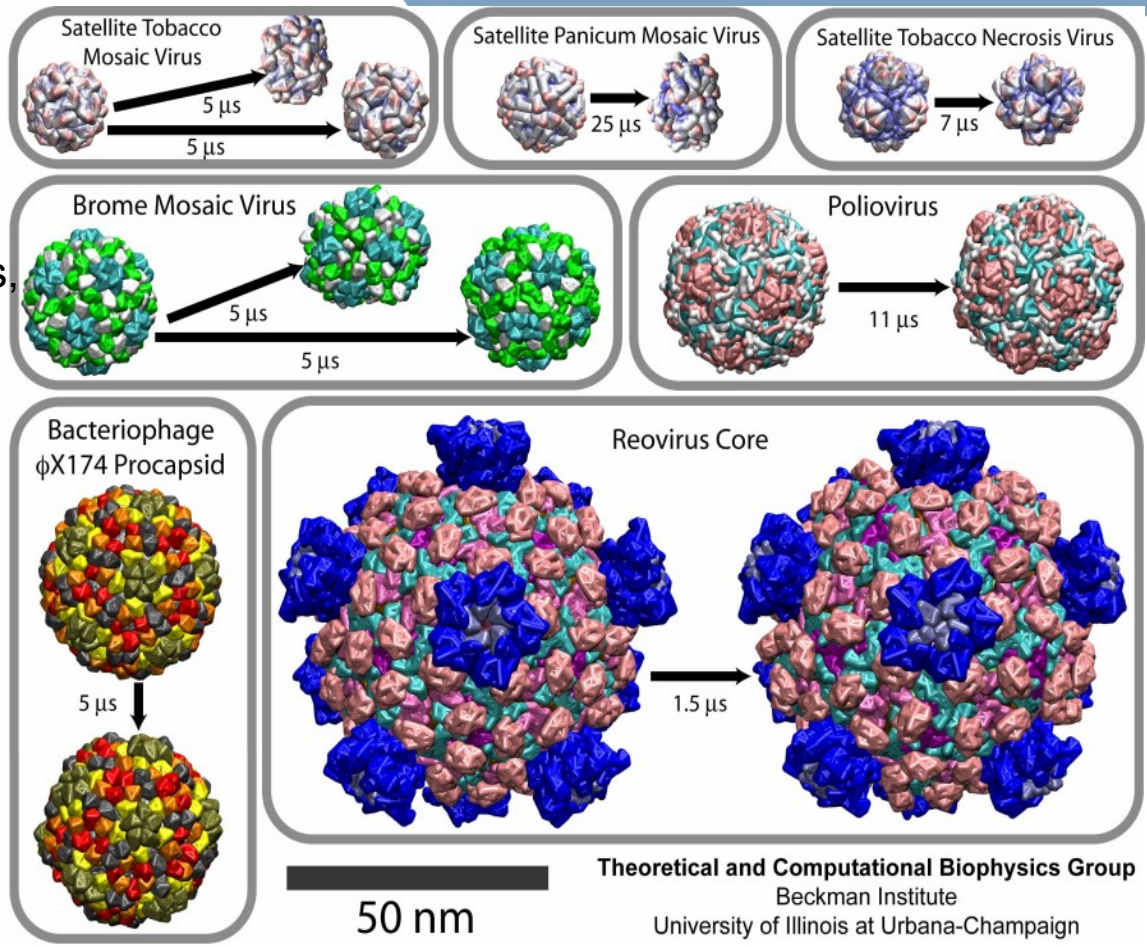

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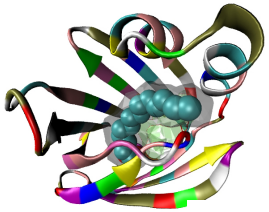
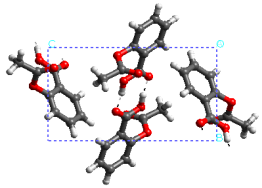
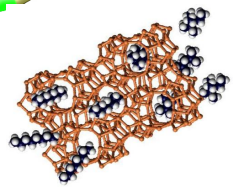
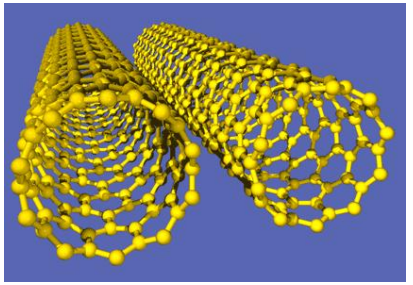






Multipole effects;
Short-range interaction

Low-dimensional systems

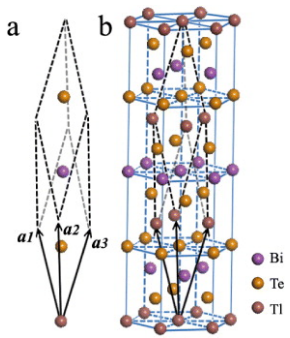


Finite-gap molecules and solids

Hybrid organic/inorganic interfaces

Metallic systems

Ionic systems



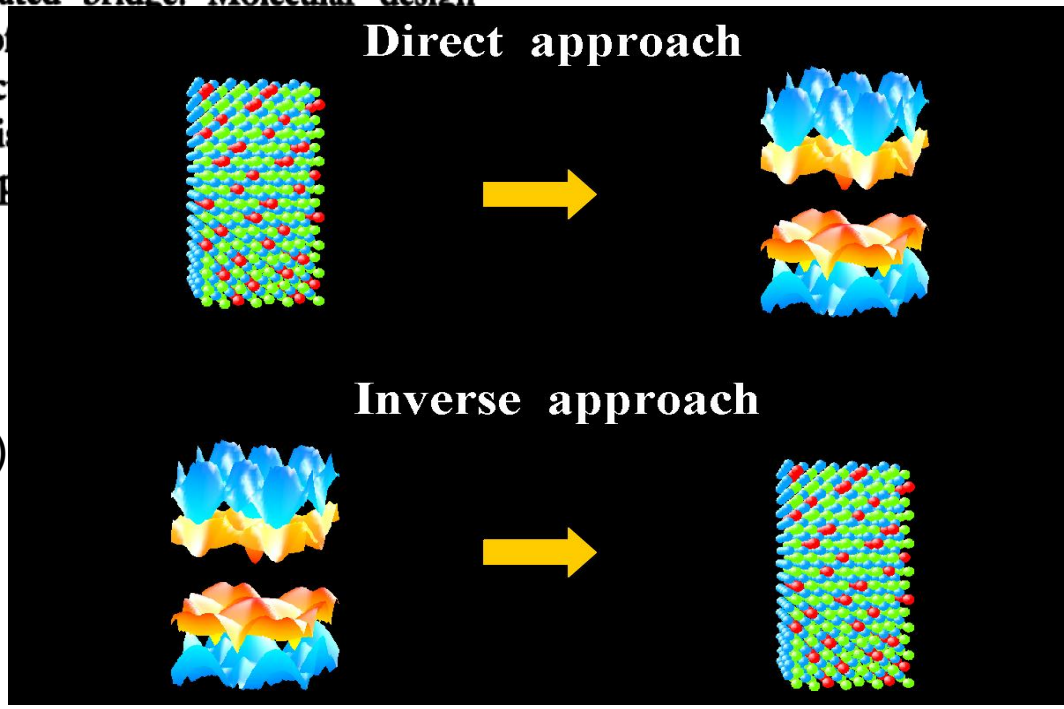
Why do we care?

Approaches for Optimizing the First Electronic Hyperpolarizability of Conjugated Organic Molecules

S. R. MARDER, D. N. BERATAN, L.-T. CHENG

A two-state, four-orbital, independent electron analysis of the first optical molecular hyperpolarizability, β, leads to the prediction that |β| maximizes at a combination of donor and acceptor strengths for a given conjugated bridge. Molecular design strategies that focus on the energetic manipulations o
for the optimization of β. The limitations of molec
bridge structures are highlighted and more promi
Experimental results supporting the validity of this a

Science (1991)



A Franceschetti & A Zunger, Nature (1999)

Many more

- Norskov et al (Stanford/DTU)
- Curtarolo&Beratan&Yang (Duke)
- Ceder (MIT)
- Wolverton (Northwestern)
- Zunger (NREL)
- Yamashita (UT)

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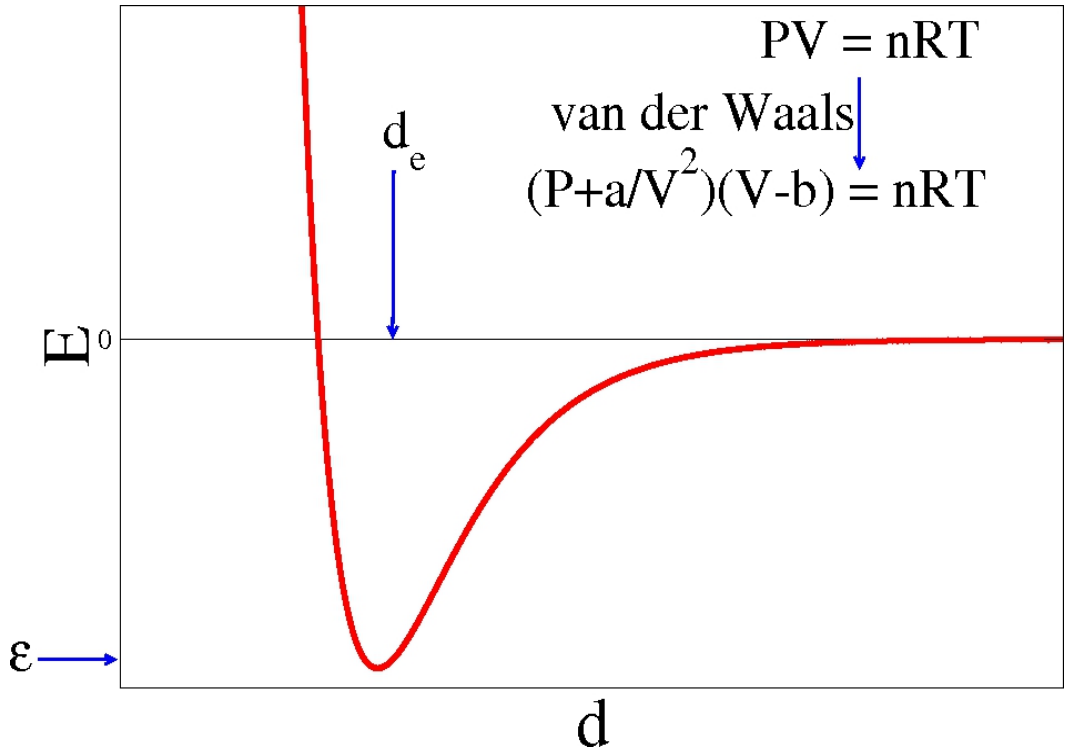
What is it?

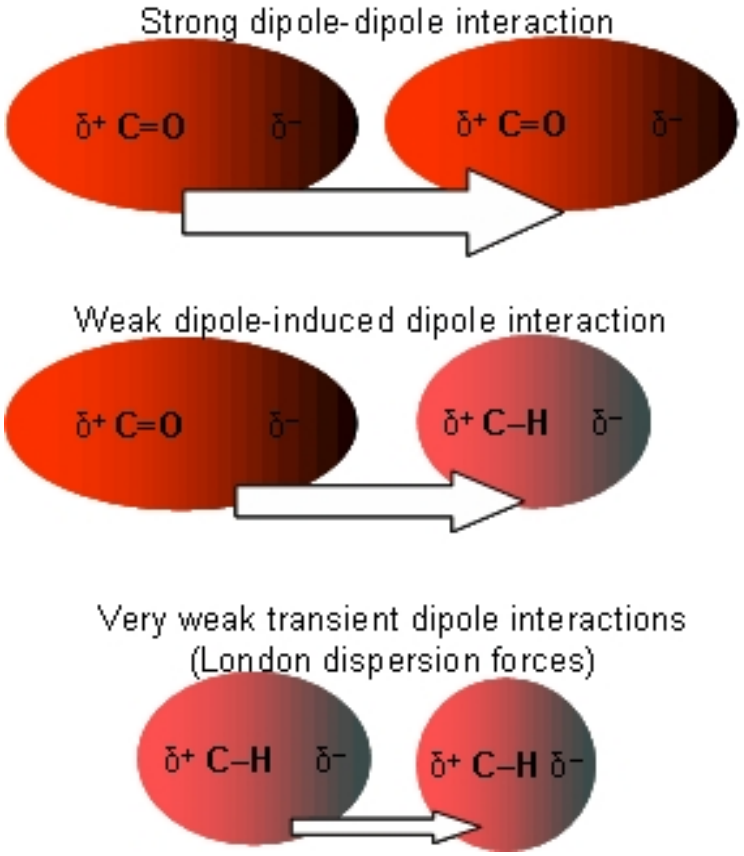


Good books

- ``Theory of intermolecular forces'' by A. J. Stone
- ``Intermolecular and surface forces'' by J. N. Israelachvili
- ``Intermolecular interactions'' by I. G. Kaplan
- ``Van der Waals forces: A Handbook for biologists, engineers and physicists'' by V. A. Parsegian

What is it?

Origin	Sign	Additive?
Electrostatic	+/-	yes
Induction	-	no
Dispersion	-	no but small
Resonance	+/-	no
Magnetic	+/- (small)	yes
Exchange	-	no
Repulsion	+	no
ChargeTransfer	-	no
Penetration	-	yes



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What's the problem with vdW?

Accuracy/
Transferability

$$H\Psi = E\Psi$$

Full CI, Quantum Monte Carlo

Correlated wavefunctions, MBPT (MP2, RPA, CCSD(T), GW, ...)

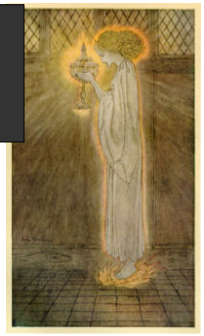
Density-functional theory (LDA/GGA, meta, hybrids, ...)

Semi-empirical methods (AM1, PM6, ZINDO, TB-DFT)

Interatomic potentials (“force fields”) (Tersoff, Brenner, Foiles, Pettifor, Karplus etc)

What's the problem with vdW?

$$H\Psi = E\Psi$$



Exact

Accuracy/
Transferability

Correlated Ψ

DFT

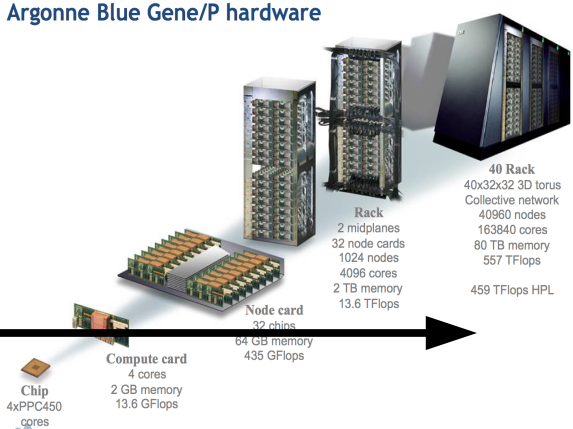
K's Nobel '98
~10k paper/year

Semi-empirical methods

Interatomic potentials

Computational Cost

Argonne Blue Gene/P hardware



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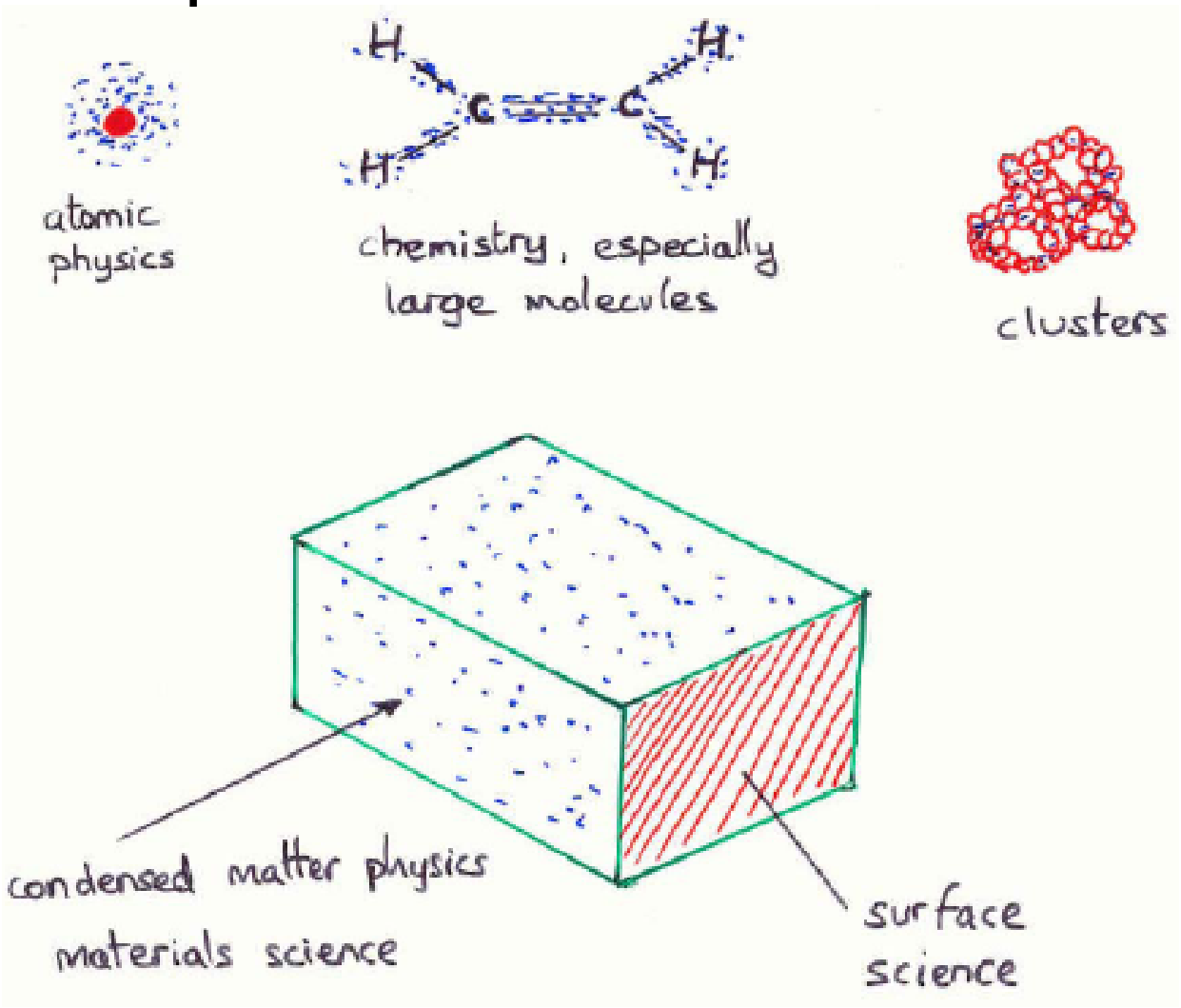
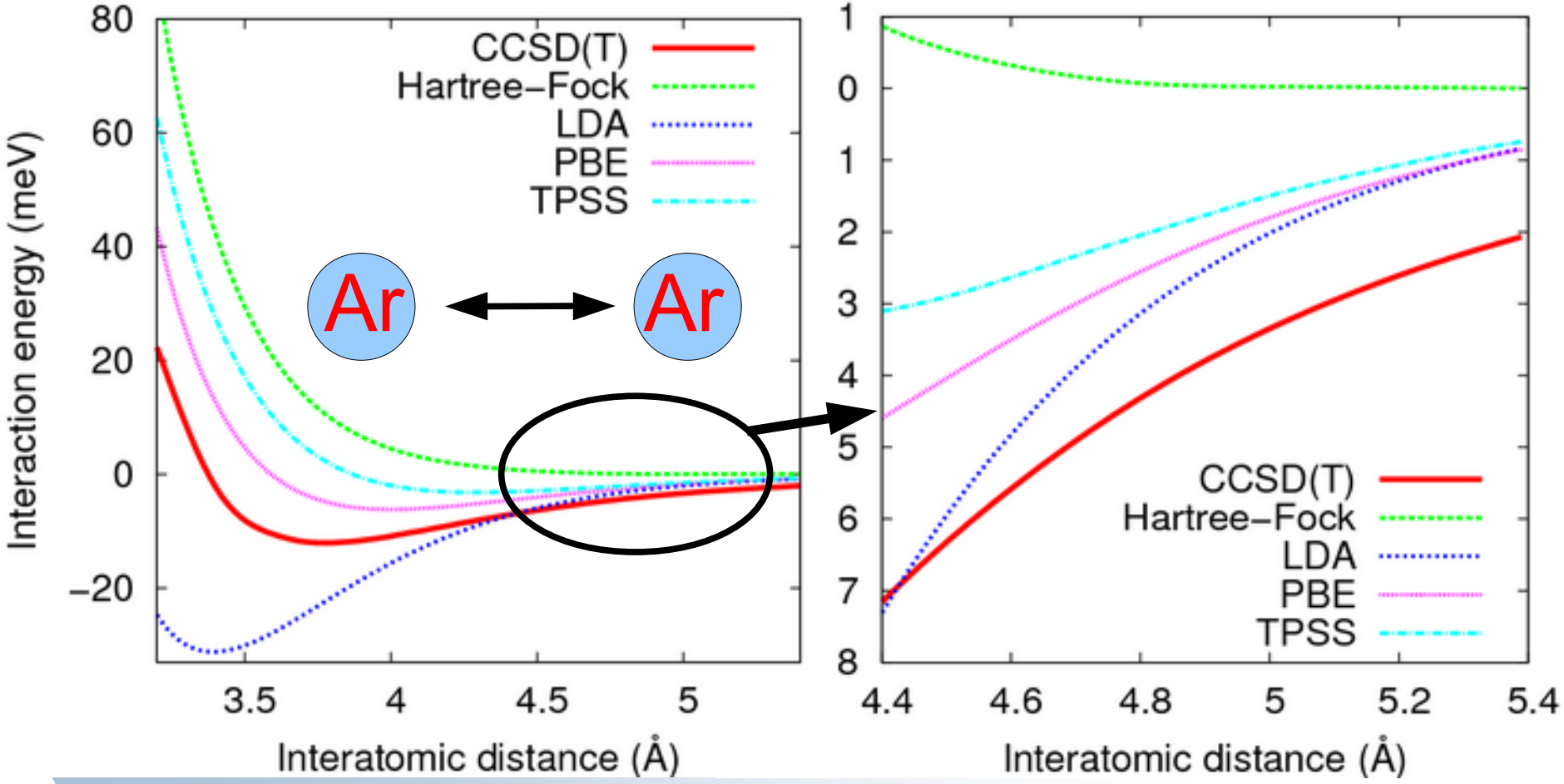


Density-functional theory (DFT)

Kieron Burke, UC Irvine

What's the problem with vdW?

$$E_{\mathrm{xc}} = E_{ex}^{\mathrm{GGA\ or\ EX}} + E_{\mathrm{corr}}^{\mathrm{LDA,GGA}} + E_{\mathrm{corr}}^{\mathrm{non-local}}$$



What's the problem with vdW?

$$E_{\mathrm{xc}} = E_{ex}^{\mathrm{GGA\ or\ EX}} + E_{\mathrm{corr}}^{\mathrm{LDA,GGA}} + E_{\mathrm{corr}}^{\mathrm{non-local}}$$

- vdW-DFT: Non-local functionals (depend explicitly on ***r*** and ***r'***) (*Dion, Langreth, Lundqvist et al.* PRL (2004)).
- Empirical atom centered potentials (*von Lilienfeld, Tavernelli, Roethlisberger, Sebastiani* PRL (2004), *DiLabio* CPL (2008))
- Empirical density functionals (*Truhlar et al.* JCP (2006), *Goddard* PNAS (2004))
- Interatomic (pairwise or beyond) dispersion corrections (Many ways)

Ahlrichs, Scoles et al (70's and 80's); *Elstner, Hobza, Frauenheim, Kaxiras* et al (2001); *Wu and Yang* ***JCP*** (2002); *Grimme* ***J. Comp. Chem.*** (2004,2006); *Johnson and Becke* ***JCP*** (2005-2007); *Silvestrelli* PRL (2008); *Tkatchenko and Scheffler* ***PRL*** (2009); and others ...

What's the problem with vdW?

Langreth-Lundqvist vdW-DFT

What's the problem with vdW?

Langreth-Lundqvist functional

$$E_{\mathrm{xc}} = E_{\mathrm{ex}}^{\mathrm{GGA}}[n(\mathbf{r})] + E_{\mathrm{corr}}^{\mathrm{LDA}}[n(\mathbf{r})] + E_{\mathrm{corr}}^{\mathrm{non-local}}[n(\mathbf{r})]$$

$$E_{\mathrm{corr}}^{\mathrm{non-local}}[n(\mathbf{r})] = \frac{1}{2}\int d^3r d^3r' n(\mathbf{r}) K(\mathbf{r},\mathbf{r}') n(\mathbf{r}')$$

Dion, Rydberg, Schroeder, Langreth, Lundqvist, ***PRL*** (2004).
Lee, Murray, Kong, Lundqvist, Langreth, ***PRB*** (2010).

What's the problem with vdW?

Langreth-Lundqvist functional (vdW-DF-04 and vdW-DF-10)

$$E_{\rm xc} = E_{\rm ex}^{\rm GGA}[n(\mathbf{r})] + E_{\rm corr}^{\rm LDA}[n(\mathbf{r})] + E_{\rm corr}^{\rm non-local}[n(\mathbf{r})]$$

$$E_{\rm corr}^{\rm non-local}[n(\mathbf{r})] = \frac{1}{2}\int d^3r d^3r' n(\mathbf{r}) K(\mathbf{r},\mathbf{r}') n(\mathbf{r}')$$

vdW-DF-04

Exchange: revPBE

Local corr.: LDA

No free parameters

C_6 error: ~ 20%

vdW-DF-10

Exchange: PW86

Local corr.: LDA

2 parameters

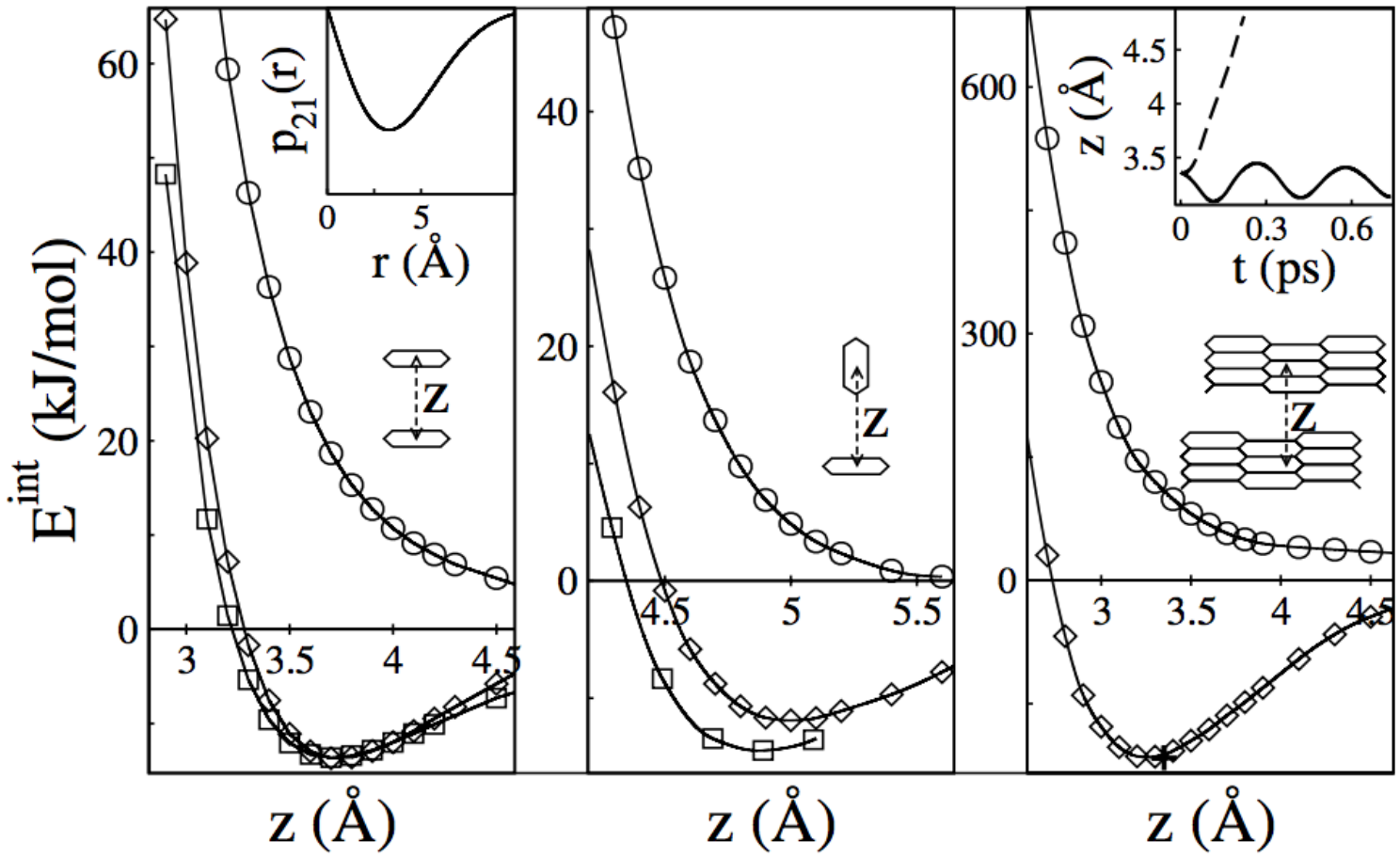
C_6 error: ~ 60%(*)

(*) *Vydrov and van Voorhis*, ***PRA*** (2010).

What's the problem with vdW?

Dispersion corrected atom centered potentials (DCACP)

What's the problem with vdW?



von Lilienfeld, Tavernelli, Sebastiani, Roethlisberger, PRL (2004)

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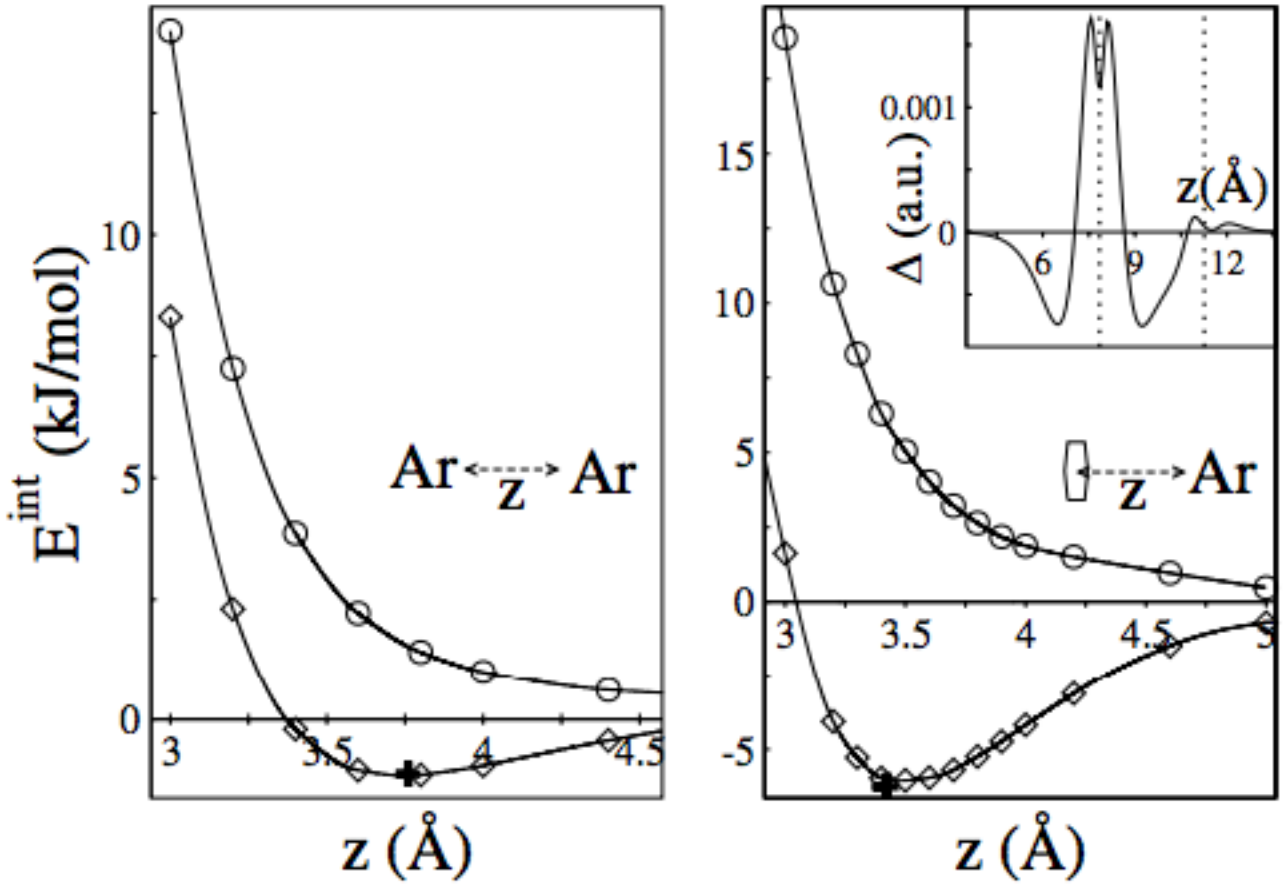

von Lilienfeld, Tavernelli, Sebastiani, Roethlisberger, PRL (2004)

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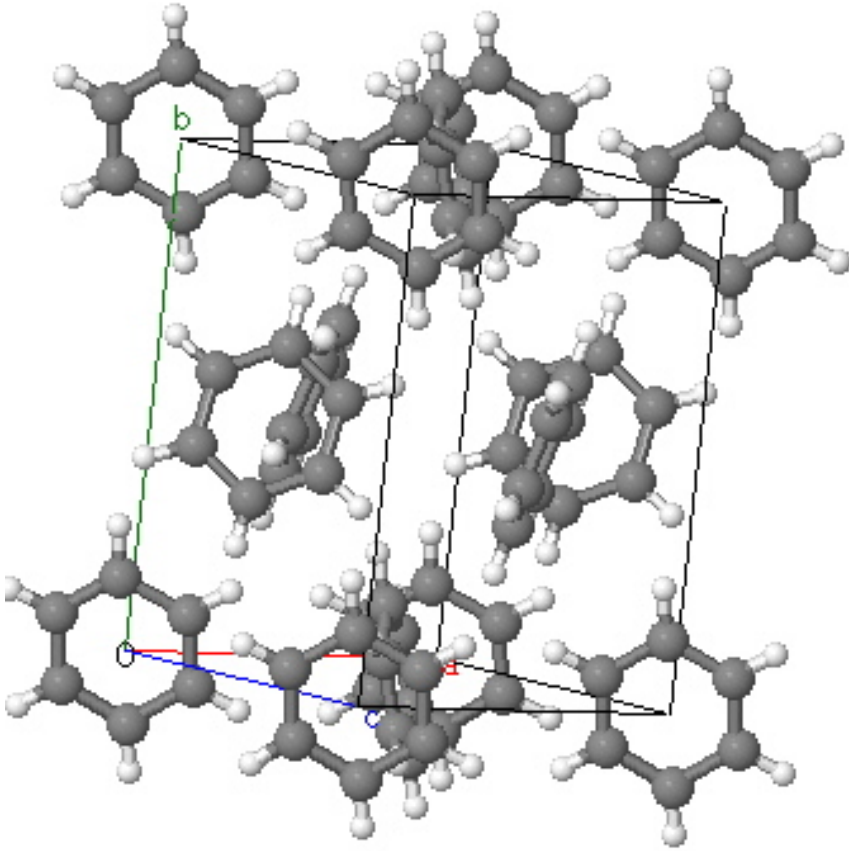
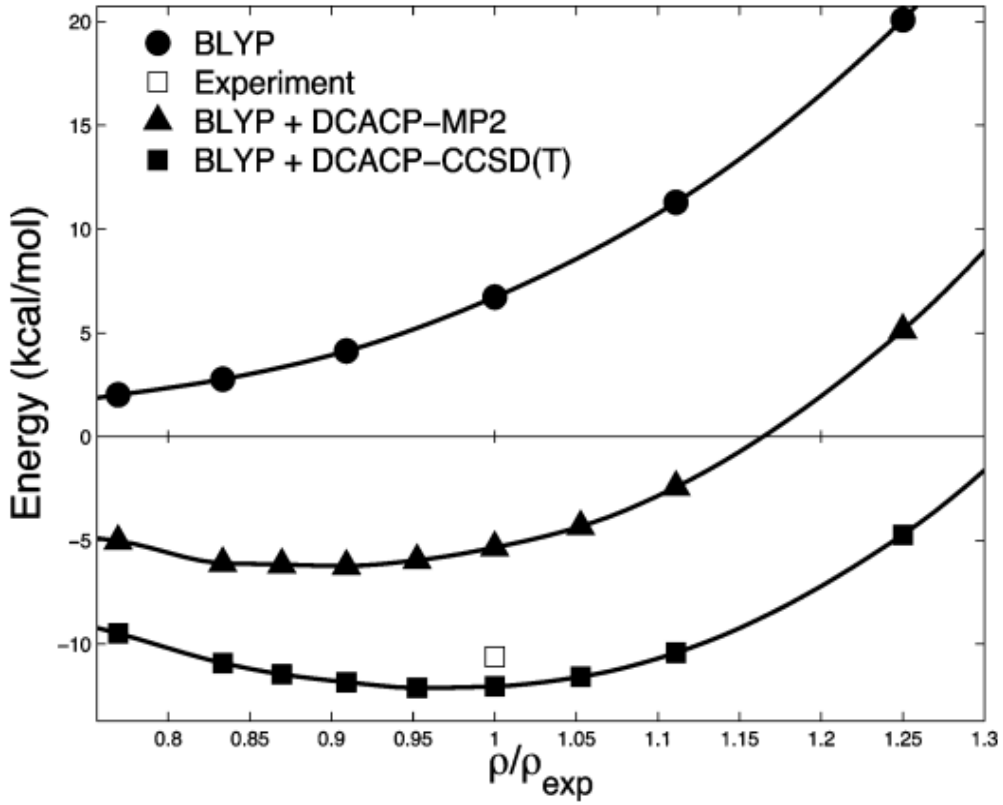
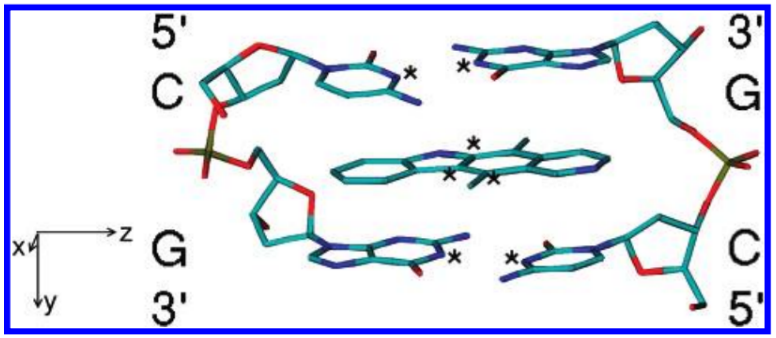


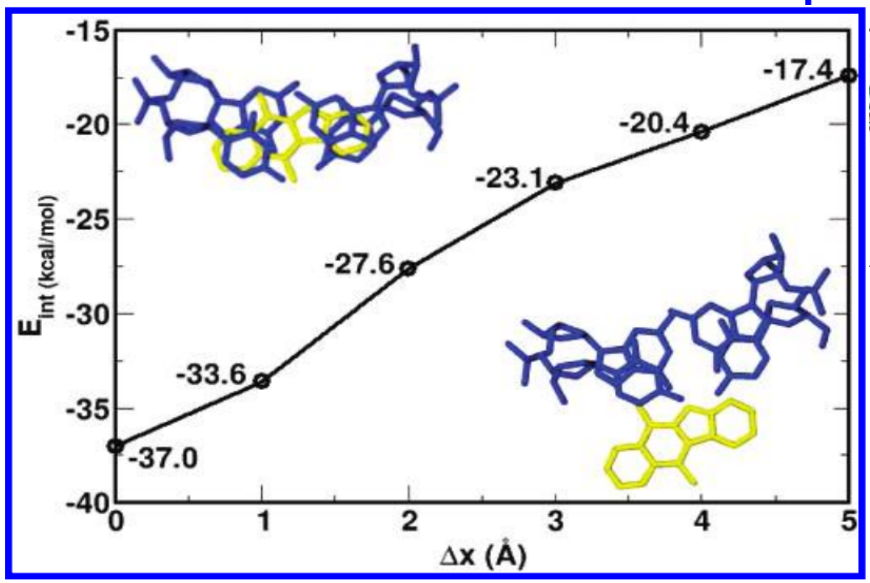


Tapavizca, Lin, von Lilienfeld, Tavernelli, Coutinho-Neto, Roethlisberger, JCTC (2007)

What's the problem with vdW?



B-DNA	$\Delta x = 0$ Å	$\Delta x = 5$ Å	Ellipticine
LUMO 2.28	LUMO 2.19	LUMO 1.55	LUMO -2.09
HOMO-1 -0.19	HOMO 0.01	HOMO-1 -0.66	HOMO -4.65
HOMO-4 -0.43	HOMO-2 -0.48	HOMO-4 -0.84	



Lin, von Lilienfeld, Coutinho-Neto, Tavernelli, Roethlisberger, JCPA (2007)

What's the problem with vdW?

Laboratory of Computational Chemistry and Biochemistry
Institute of Chemical Sciences and Engineering
Swiss Federal Institute of Technology EPF Lausanne
Group Röthlisberger

Ho Home Adresse	Gr Group members	Re Research QM/MM	Pu Publications	Op Open position	Im Gallery of Images	Se Seminars	Lb Library	Li Links
Co Course	It Internal	Dc Research DCACP						

Dispersion-Corrected Atom-Centered Potentials in Goedecker Format

Elements H, C, N, O, He, Ne, Ar and Kr:

Phys. Rev. B, 75, 205131 (2007) **DOI: 10.1103/PhysRevB.75.205131**

Element S:

J. Chem. Theory Comput., 5(1), 23 (2008) **DOI: 10.1021/ct800299y**

BLYP / PBE / BP / Misc

H																	**He**
Li	Be											B	**C**	**N**	**O**	F	**Ne**
Na	Mg											Al	Si	**P**	**S**	Cl	**Ar**
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	**Kr**
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Roethlisberger group: http://lcbcpc21.epfl.ch/DCACP/DCACP.html

What's the problem with vdW?

Pair-wise corrected DFT

$$E_{\mathrm{xc}} = E_{ex}^{\mathrm{GGA\ or\ EX}} + E_{\mathrm{corr}}^{\mathrm{LDA,GGA}} + E_{\mathrm{corr}}^{\mathrm{non-local}}$$

$$E^{vdW}(R) = -\left(f_6(R)\frac{C_6}{R^6} + f_8(R)\frac{C_8}{R^8} + f_{10}(R)\frac{C_{10}}{R^{10}} + \ldots \right)$$

$$E_{\mathrm{vdW}}^{(2)} = -\frac{C_6^{\mathrm{AB}}}{R_{\mathrm{AB}}^6} \qquad C_6^{\mathrm{AB}} = \frac{3}{\pi}\int \alpha_{\mathrm{A}}(i\omega)\alpha_{\mathrm{B}}(i\omega)d\omega$$

What's the problem with vdW?

Pair-wise corrected DFT

Grimme's D1,D2 (2004-2006): Parameterization for many elements in the periodic table

- Highly empirical, some very *ad hoc* approximations

Jurečka, Hobza *et al.* (2007): Accurate parameterization for organic molecules

- Better theoretical ground, but still very empirical

Johnson and Becke (2005-2008), Silvestrelli (2008): On-the-fly C_6 and vdW radii from HF or DFT orbitals

- Reduced empiricism, errors of ~ 20%-40% in C_6 coefficients

Tkatchenko and Scheffler (2009): On-the-fly C_6 coefficients and vdW radii from ground-state electron density

- First-principles C_6 accurate to **5%**

What's the problem with vdW?

TS-vdW method: Atomic vdW parameters from first principles

Dissociative asymptotics with an accuracy of 5%

Transparent partitioning of vdW coefficients over atoms

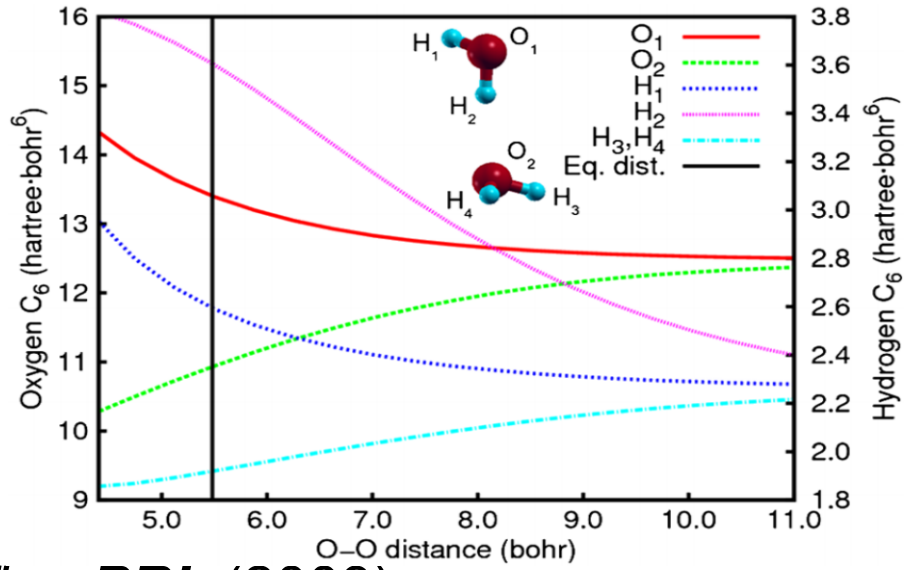
On-the-fly atomic polarizability ratio proportional to atomic volume ratio

No computational overhead

Valid for entire periodic table

$$C_{6AA}[n(\mathbf{r})] = \left(\frac{V_A[n(\mathbf{r})]}{V_A^{free}[n^{free}(\mathbf{r})]} \right)^2 C_{6AA}^{free}$$

$$C_{6AB} = \frac{2 C_{6AA} C_{6BB}}{[\frac{\alpha_B^0}{\alpha_A^0} C_{6AA} + \frac{\alpha_A^0}{\alpha_B^0} C_{6BB}]}$$



A. Tkatchenko and M. Scheffler, ***PRL*** (2009)

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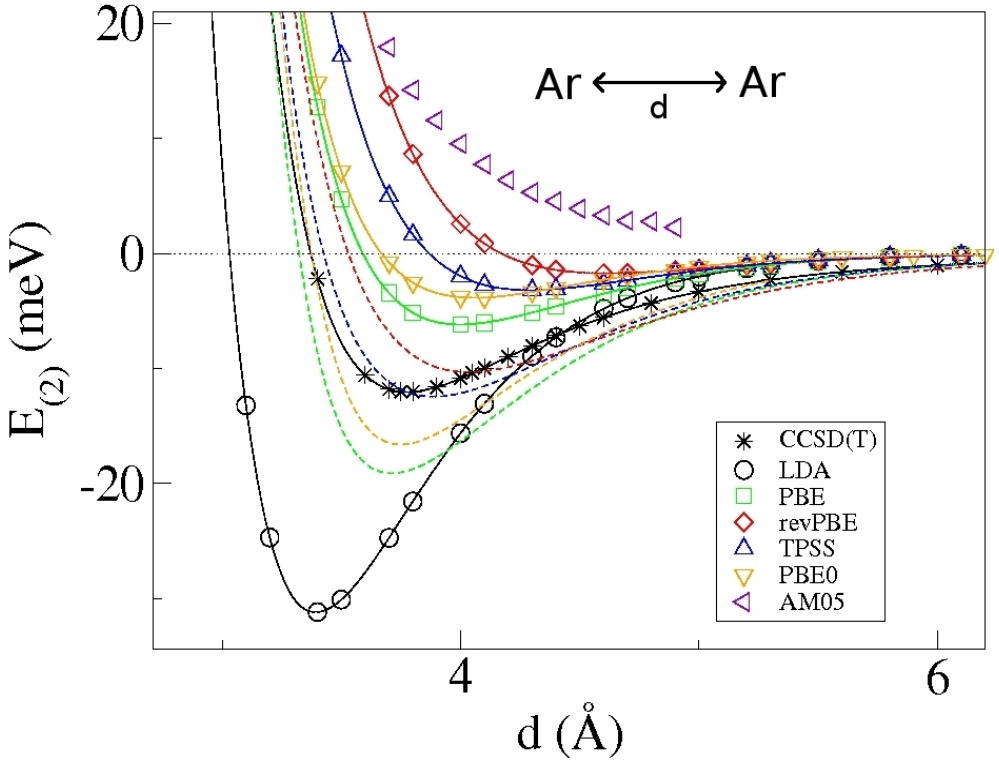
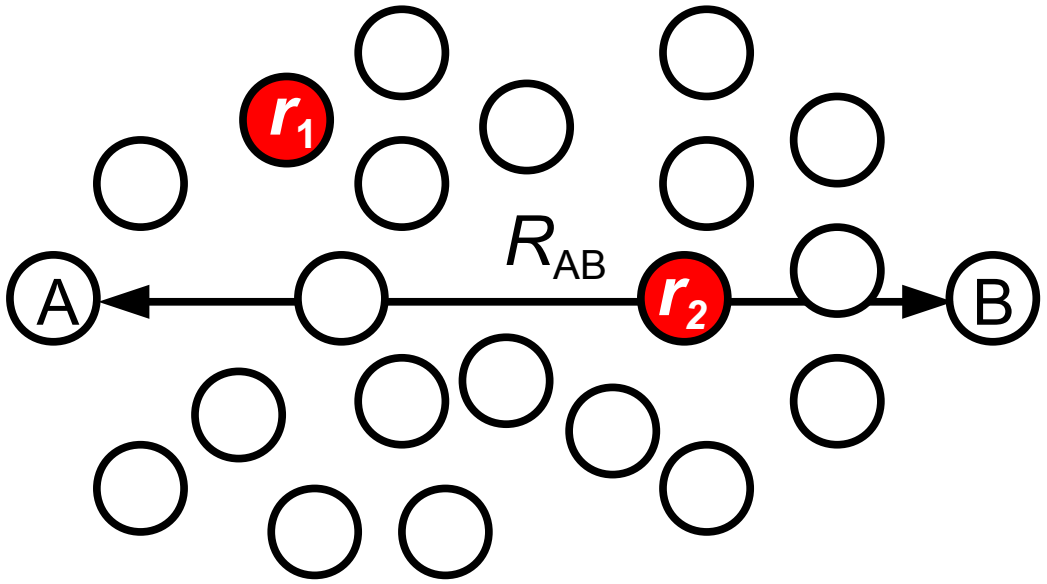
Many-body dispersion in DFT

Pair-wise corrected DFT



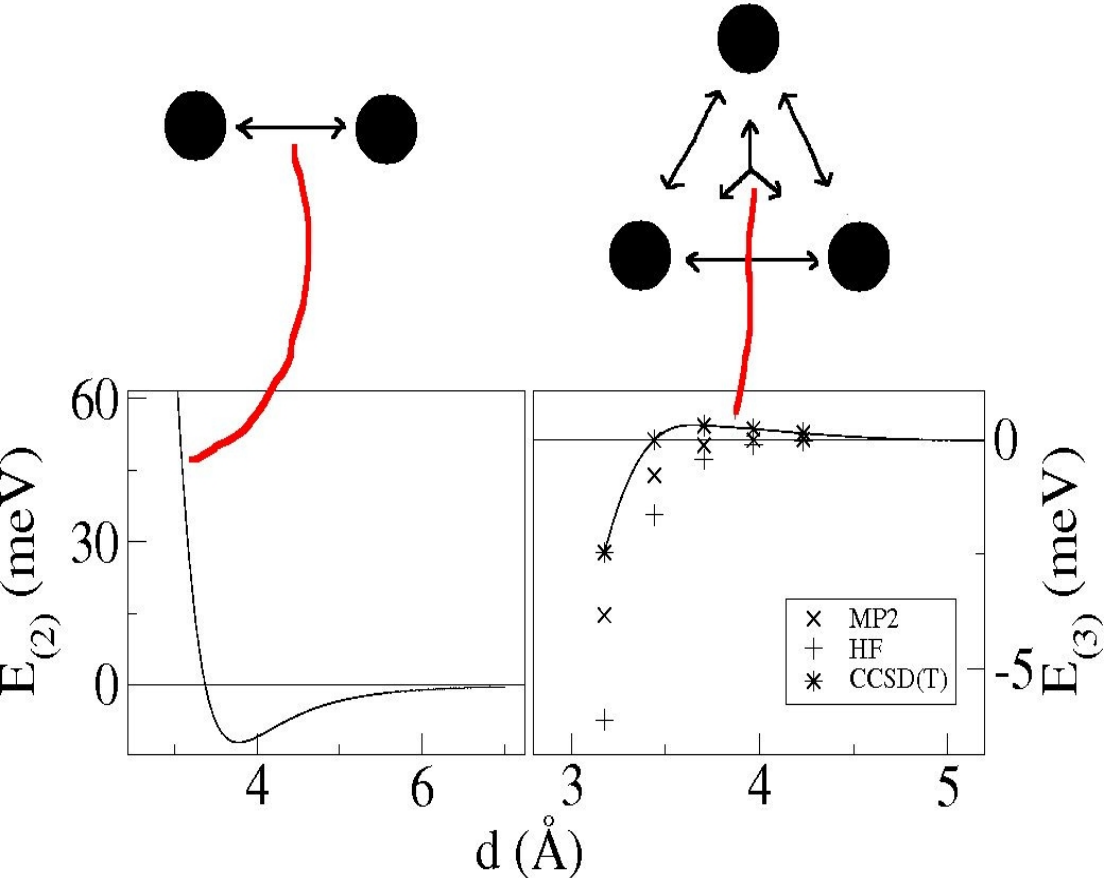
Many-body dispersion in DFT

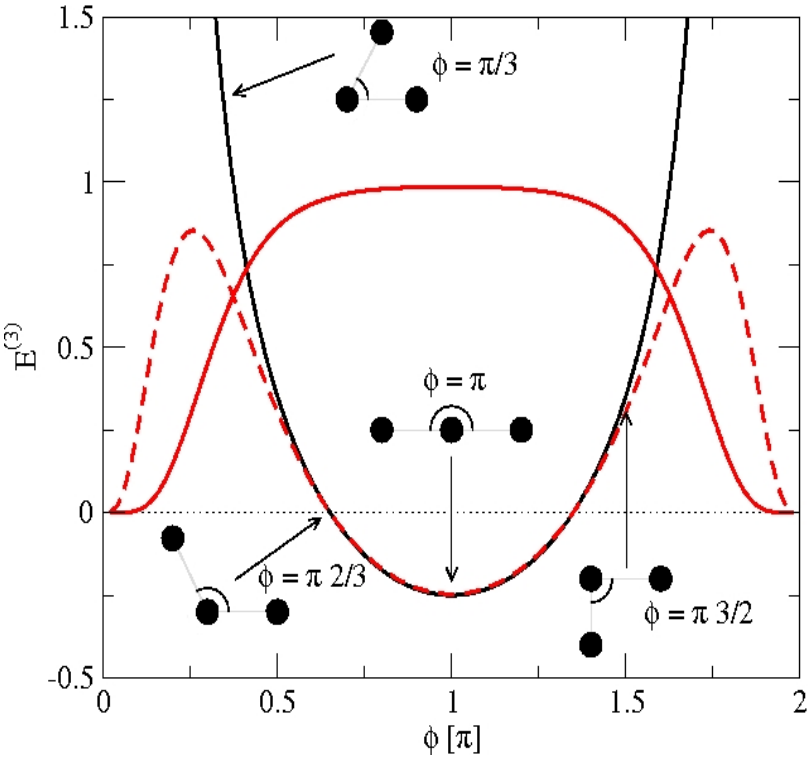
Coulomb Screening



Many-body vdW Energy

Many-body dispersion in DFT

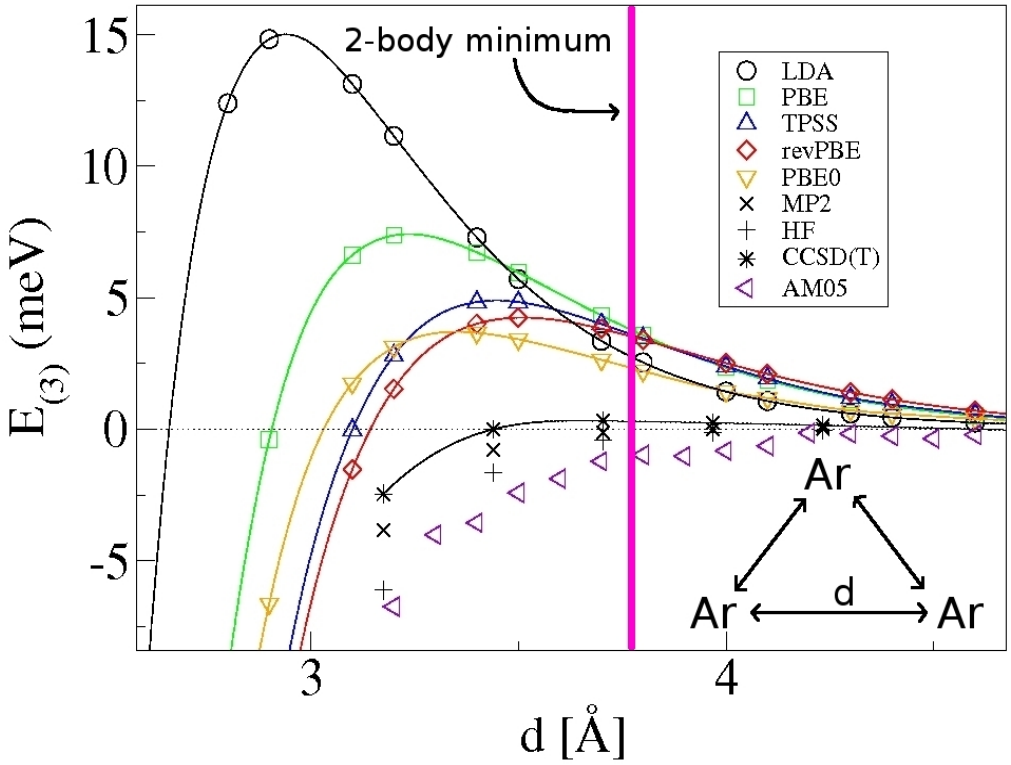


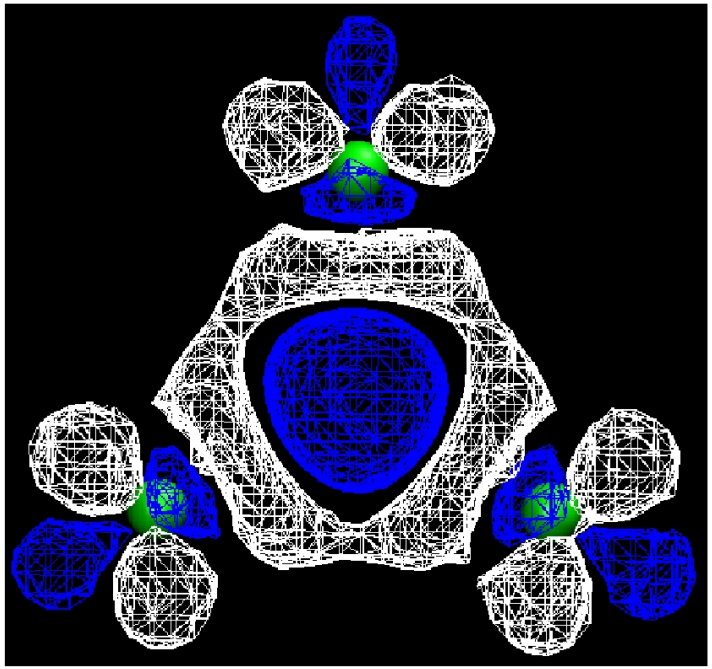


Axilrod & Teller *J Chem Phys* (1943); Muto *J Phys-Math Soc Japan* (1943)

$$E_{(3)}[A,B,C] \quad = \quad C9_{ABC}\,\frac{3\,\cos[\gamma_{AB}]\cos[\gamma_{AC}]\cos[\gamma_{BC}]+1}{\mathrm{d}_{AB}^3\mathrm{d}_{AC}^3\mathrm{d}_{BC}^3}+\ldots$$

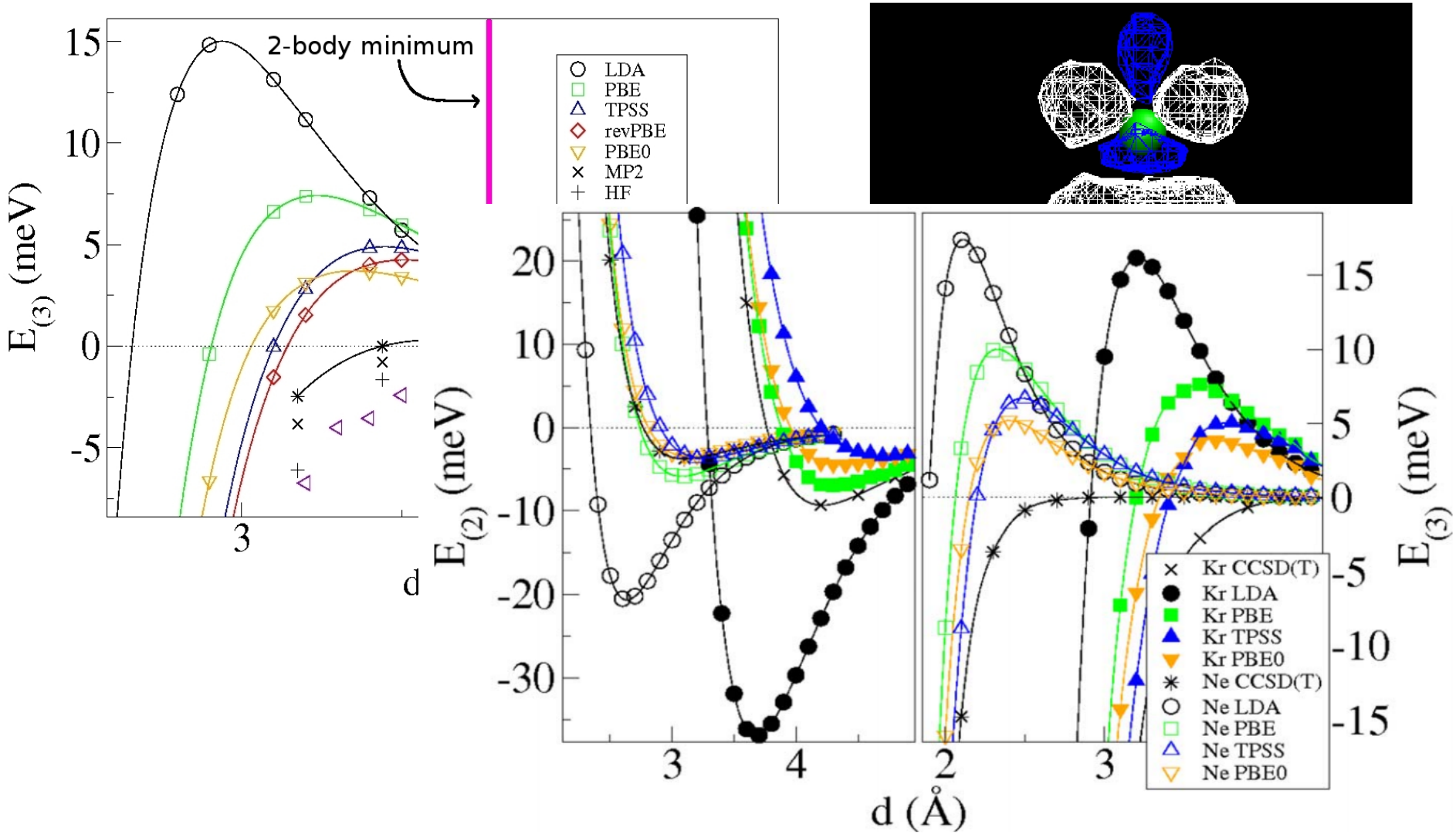
Many-body dispersion in DFT





Tkatchenko & von Lilienfeld, PRB (2008)

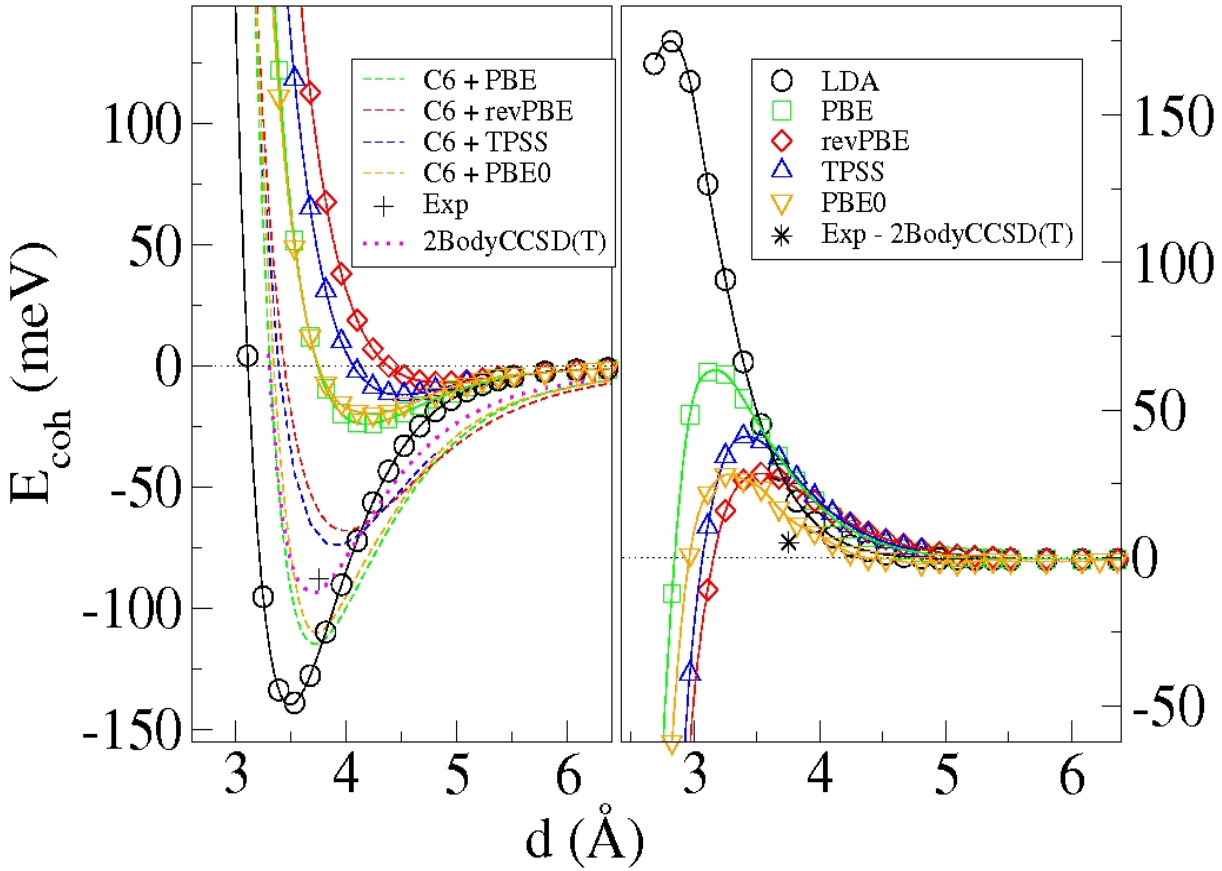
Many-body dispersion in DFT

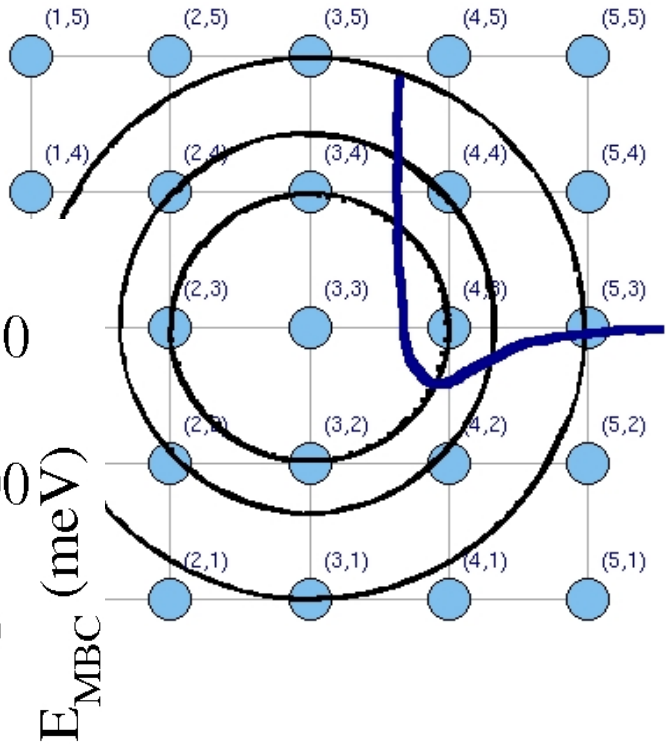


Tkatchenko & von Lilienfeld, PRB (2008)

Many-body dispersion in DFT

For rare gas crystals, experimental
MBC estimated to be up to 10% of cohesive energy





Functional	MBC
LDA	35 %
PBE	50 %
TPSS	80 %

Tkatchenko & von Lilienfeld, PRB (2008)

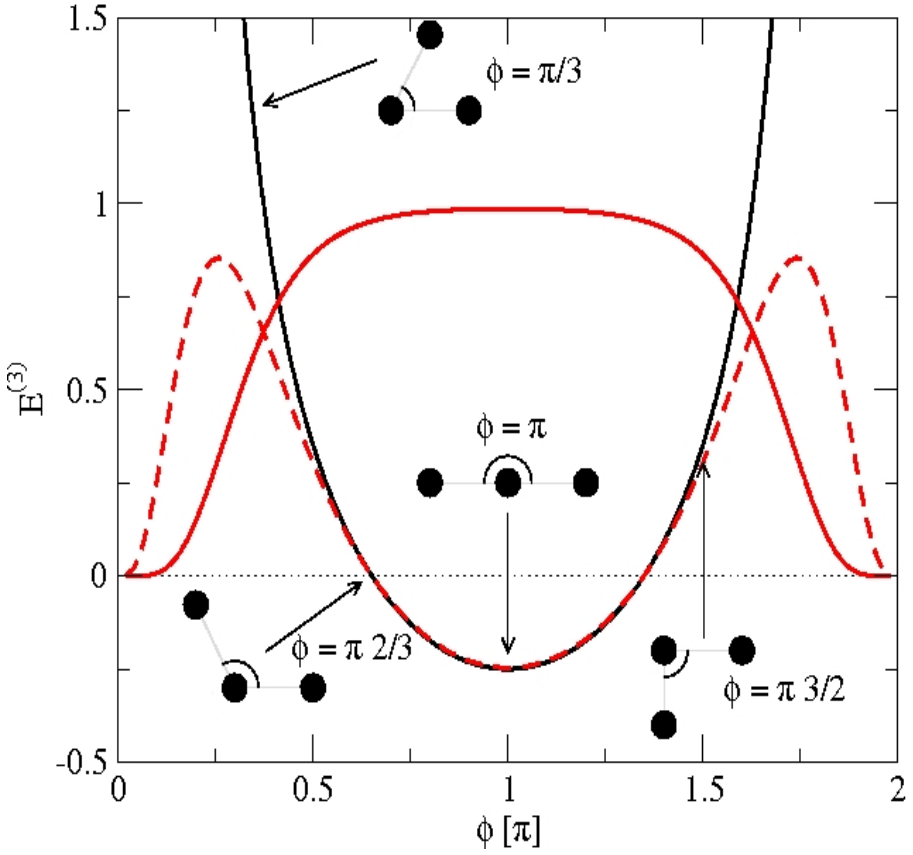
Overview

- Tutorial (first half)
  - Why do we care?
  - What is it?
  - What's the problem with vdW?
- Recent contributions (second half)
  - Many-body dispersion in DFT
  - 3-body dispersion effects
  - Many-body dispersion effects

3-body dispersion effects

Axilrod & Teller *J Chem Phys* (1943); Muto *J Phys-Math Soc Japan* (1943)

$$E_{(3)}[A,B,C] \quad = \quad C9_{ABC}\,\frac{3\,\cos[\gamma_{AB}]\cos[\gamma_{AC}]\cos[\gamma_{BC}]+1}{\mathrm{d}_{AB}^3\mathrm{d}_{AC}^3\mathrm{d}_{BC}^3}+\ldots$$



von Lilienfeld & Tkatchenko, JCP (2010)

3-body dispersion effects

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$$C9_{IJK}=\frac{3}{\pi}\int_0^\infty d\omega\alpha_I(i\omega)\alpha_J(i\omega)\alpha_K(i\omega) \qquad C6_{IJ}=\frac{3}{\pi}\int_0^\infty d\omega\alpha_I(i\omega)\alpha_J(i\omega)$$

$$C9_{IJK}=\frac{8}{3}\frac{P_IP_JP_K(P_I+P_J+P_K)}{(P_I+P_J)(P_J+P_K)(P_K+P_I)},$$

$$P_I=C9_{III}\frac{\alpha_{0,J}\alpha_{0,K}}{\alpha_{0,I}^2}$$

$$C9_{III}[n(\mathbf{r})]\approx\left(\frac{V_I[n(\mathbf{r})]}{V_I^{\mathrm{free}}[n^{\mathrm{free}}(\mathbf{r})]}\right)^3 C9_{III}^{\mathrm{free}} \qquad \frac{V_I[n(\mathbf{r})]}{V_I^{\mathrm{free}}[n^{\mathrm{free}}(\mathbf{r})]}=\left(\frac{\int d\mathbf{r}r^3n_I(\mathbf{r})}{\int d\mathbf{r}r^3n_I^{\mathrm{free}}(\mathbf{r})}\right)$$

von Lilienfeld & Tkatchenko, JCP (2010)

Tkatchenko&Scheffler, PRL (2009)

3-body dispersion effects

Atom	α	C_6	C_9	R_{vdW}
H^{free}	4.50	6.5	21.6	3.10
H^{s}	2.75	2.42	4.91	2.63
He	1.38	1.46	1.47	2.65
C^{free}	12.0	46.6	373	3.59
C^{sp}	9.73	30.6	199	3.35
C^{sp^2}	9.67	30.3	195	3.34
C^{sp^3}	8.64	24.1	139	3.22
N^{free}	7.40	24.2	117	3.34
N^{sp^2,sp^3}	6.36	17.9	74.4	3.18
O^{free}	5.40	15.6	52.6	3.19
O^{sp^2}	4.92	13.0	39.8	3.09
O^{sp^3}	4.81	12.4	37.1	3.07
F^{free}	3.80	9.52	24.2	3.04
F^{sp^3}	3.46	7.89	18.3	2.95
Ne^{free}	2.67	6.38	12.0	2.91
Si^{free}	37.0	305	8550	4.20
Si^{sp^3}	25.6	146	2846	3.72
P^{free}	25.0	185	3561	4.01
S^{free}	19.6	134	1925	3.86
S^{sp^3}	18.2	115	1532	3.76
Cl^{free}	15.0	94.6	1014	3.71
Cl^{sp^3}	14.6	89.4	932	3.68
Ar	11.1	64.3	518	3.55
Br^{free}	20.0	162	2511	3.93
Br^{sp^3}	19.5	155	2340	3.90
Kr	16.8	130	1572	3.82

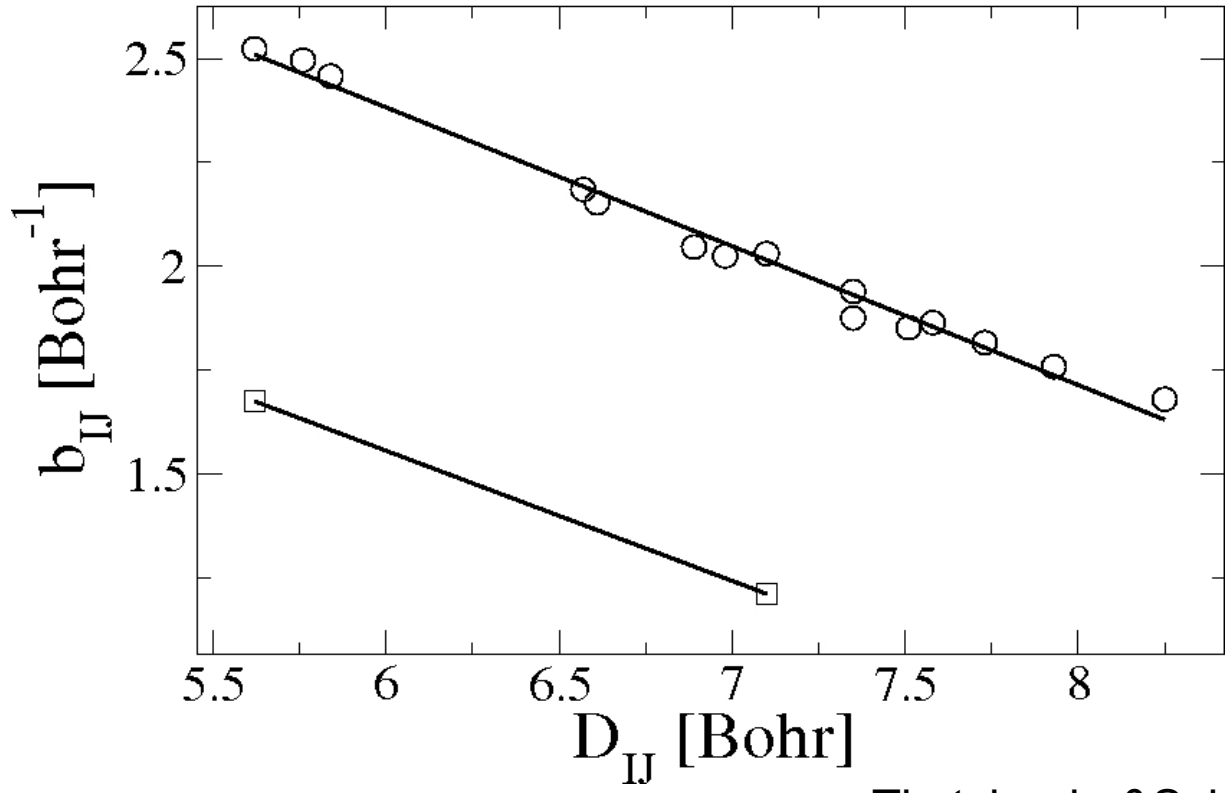
von Lilienfeld & Tkatchenko, JCP (2010)

3-body dispersion effects

Damping according to Tang&Toennis

$$f_6^d(R_{IJ}) = 1 - e^{-b_{IJ}R_{IJ}} \sum_{k=0}^{n=6} \frac{(b_{IJ}R_{IJ})^k}{k!}$$

$$f_{\mathrm{ATM}}^d(R_I,R_J,R_K) = f_6'(R_{IJ}) \times f_6'(R_{IK}) \times f_6'(R_{JK})$$



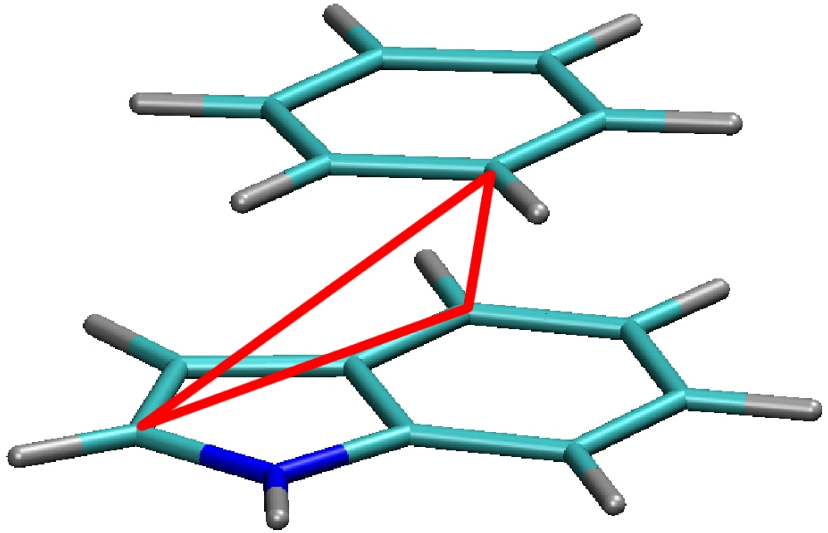
von Lilienfeld & Tkatchenko, JCP (2010)

Tkatchenko&Scheffler, PRL (2009)

3-body dispersion effects

TABLE II. Interatomic $E^{(2)}$ and $E^{(3)}$ contributions to S22 benchmark data set results in kcal/mol. CCSD(T) results from S22 data set in Ref. 9.

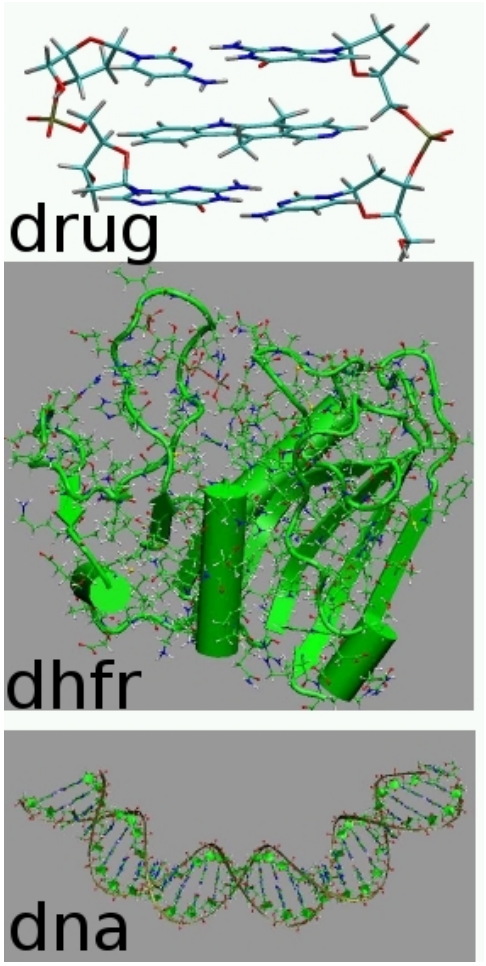
No.		$E^{(2)}$	$E^{(3)}$	CCSD(T)
1	(NH_3) dimer (C_{2h})	−1.43	0.00	−3.17
2	(H_2O) dimer (C_s)	−1.80	−0.01	−5.02
3	Formic acid dimer	−7.87	0.02	−18.61
4	Formamide dimer (C_{2h})	−5.69	0.02	−15.96
5	Uracil dimer (C_{2h})	−7.03	−0.07	−20.65
6	2-pyridoxine-2-aminopyridine (C_1)	−7.16	−0.02	−16.71
7	Adenine-thymine WC	−7.54	−0.04	−16.37
8	(CH_4) dimer (D_{3d})	−0.68	0.02	−0.53
9	(C_2H_4) dimer (D_{2d})	−1.96	0.05	−1.51
10	Benzene-CH_4 (C_3)	−1.97	0.14	−1.50
11	Benzene dimer (C_{2h})	−5.64	0.68	−2.73
12	Pyrazine dimer (C_s)	−5.92	0.60	−4.42
13	Uracil dimer (C_2)	−8.90	0.96	−10.12
14	Indole-benzene (C_1)	−8.48	1.10	−5.22
15	Adenine-thymine stack	−13.04	1.54	−12.23
16	Ethene-ethine (C_{2v})	−0.93	0.01	−1.53
17	Benzene-H_2O (C_s)	−2.35	0.15	−3.28
18	Benzene-NH_3 (C_s)	−2.15	0.14	−2.35
19	Benzene-HCN (C_s)	−2.84	0.15	−4.46
20	Benzene dimer (C_{2v})	−3.61	0.21	−2.74
21	Indole-benzene T-shape	−5.24	0.30	−5.73
22	Phenol dimer (C_1)	−5.18	0.19	−7.05



von Lilienfeld & Tkatchenko, JCP (2010)

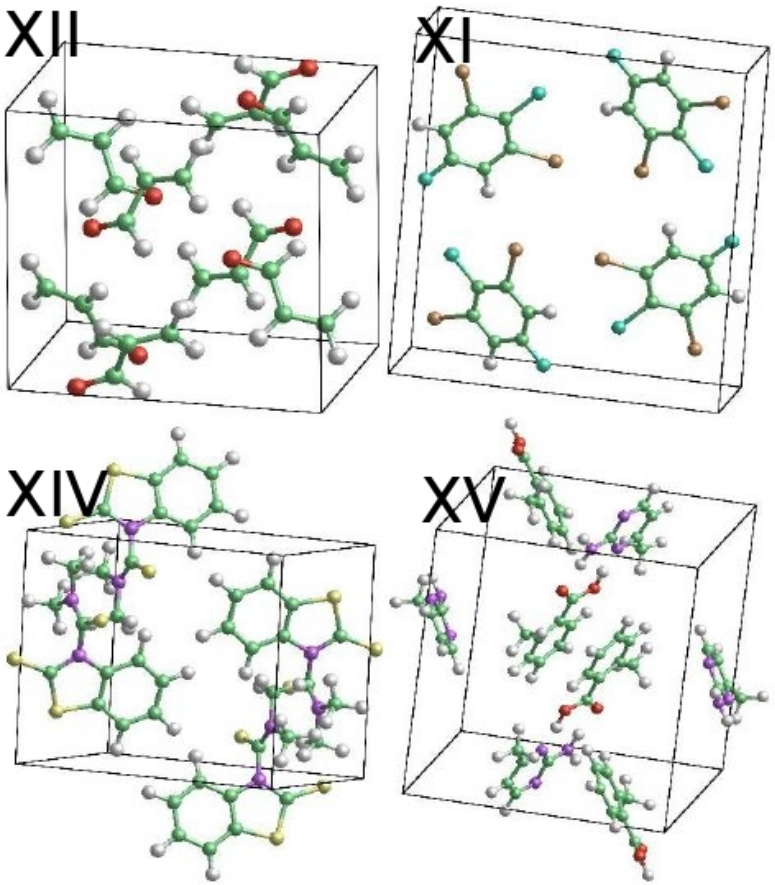
3-body dispersion effects

System	E	$E^{(3)}$	$E^{(2)}$
Ar crystal	-2.03[a]	0.07	-2.17
benzene crystal	-10.6[b]	1.67	-16.1
diamond	-171.3[c]	2.03	-50.5
ice Ih	-14.1[d]	0.04	-2.96
bi-graphene	-1.20[e]	0.61	-2.13
$(C_{60})_2$	-7.33[f]	1.02	-11.4
drug	-37.0[g]	8.90	-57.0
Ala_{10}(α-FES)/residue	-0.96[h]	0.44	-5.95
dhfr/amino acid[i]	-	1.60	-320.0
dna/base[i]	-	1.45	-241.67



von Lilienfeld & Tkatchenko, JCP (2010)

3-body dispersion effects



# Polymorph	PW91+vdW[a]	PBE+vdW[b]	$E^{(2)}$	$E^{(3)}$
XII				
1	0.0	0.0	0.0	0.0
2	0.28	0.58	1.66	-0.07
3	0.47	0.40	-1.07	0.06
XI				
1	0.0	0.0	0.0	0.0
2	0.32	0.59	0.70	-0.09
3	0.34	0.88	1.77	-0.21
XIV				
1	0.0	0.0	0.0	0.0
2	0.47	1.05	1.94	-0.32
3	1.05	0.98	1.25	-0.13
XV				
1	0.0	0.0	0.0	0.0
2	0.50	0.35	1.54	0.02
3	0.59	0.75	2.72	-0.14

von Lilienfeld & Tkatchenko, JCP (2010)

Overview

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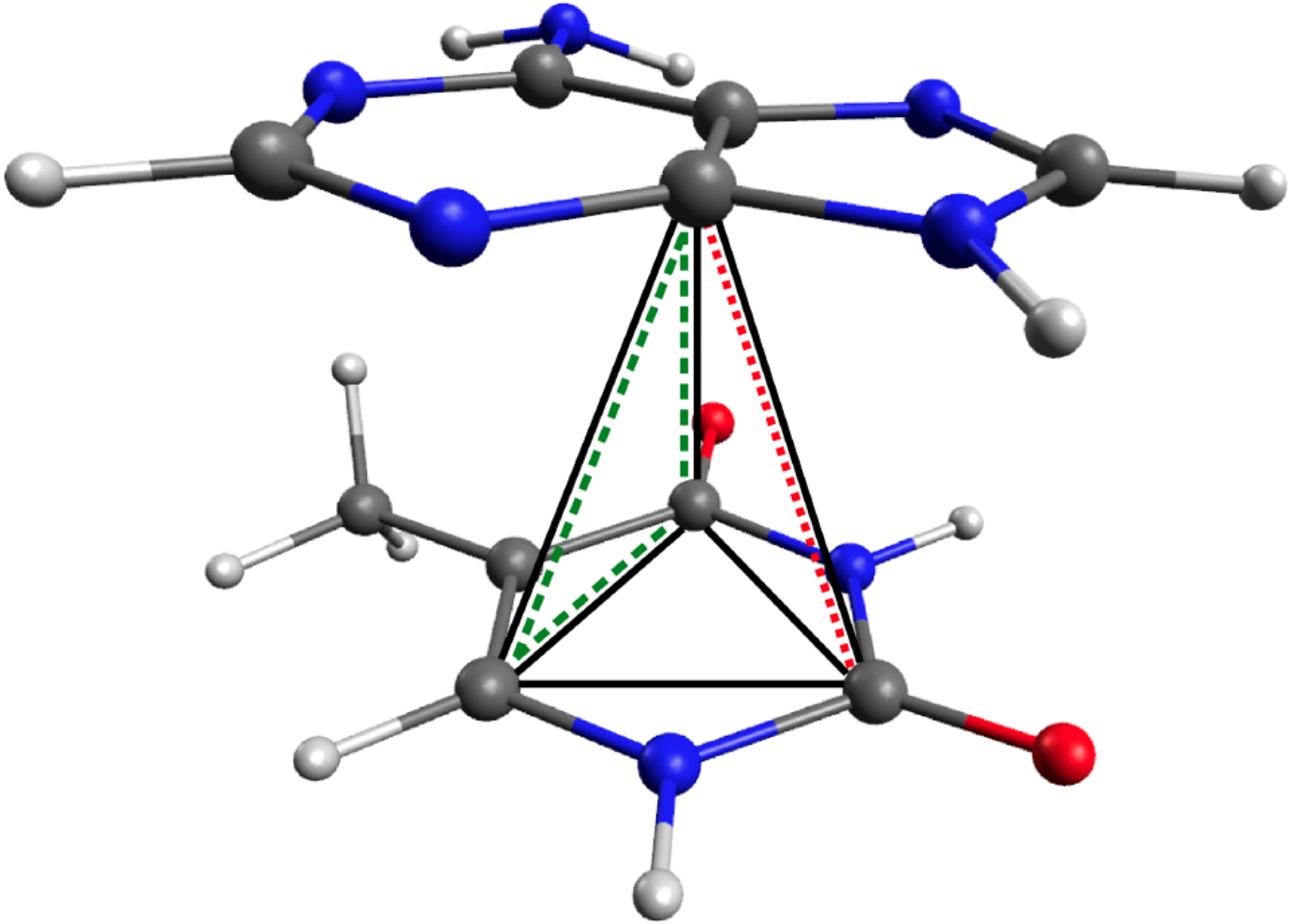
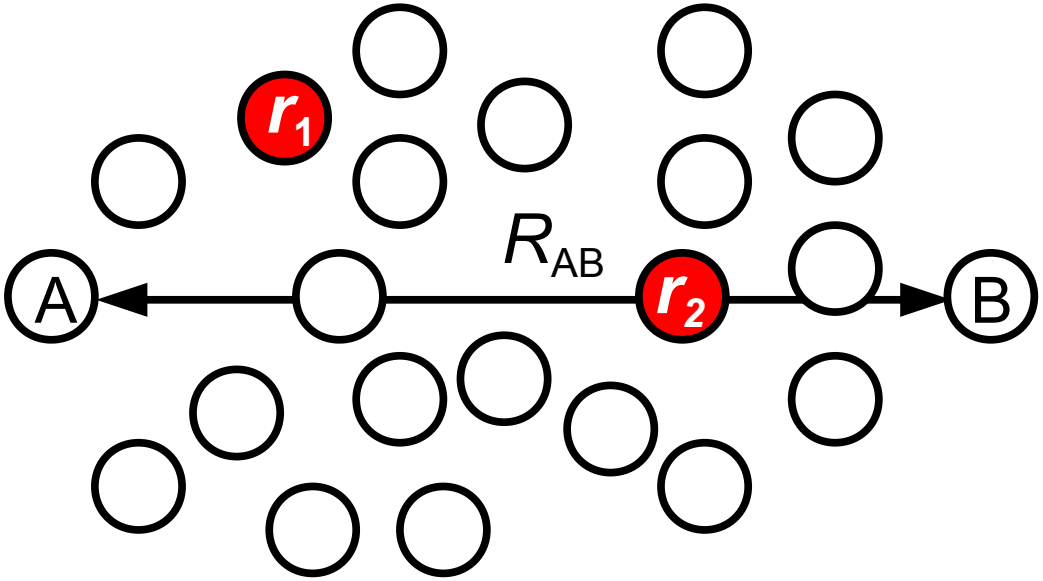
Many-body dispersion effects



Tkatchenko, von Lilienfeld, DiStasio, submitted to PNAS (2012)

Many-body dispersion effects

Coulomb Screening



Many-body vdW Energy

Use DFT+MBD method

A. Tkatchenko, R. A. DiStasio Jr., R. Car, M. Scheffler, PRL (2012).

TS-vdW method

$$\alpha_A^0 = \alpha_A^0[n(\mathbf{r})]; \quad \omega_A^0 = \omega_A^0[n(\mathbf{r})]$$

Self-consistent electrostatic screening (SCS)

$$\alpha_p(i\omega) = \alpha_p^{\mathrm{TS}}(i\omega) + \alpha_p^{\mathrm{TS}}(i\omega) \sum_{q \neq p}^{N} \mathcal{T}_{pq} \alpha_q(i\omega)$$

Many-body vdW energy for a system of coupled oscillators (CFDM)

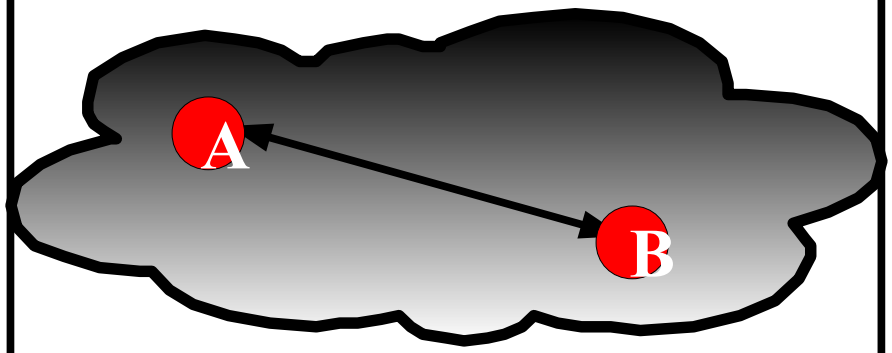
$$H = -\frac{1}{2}\sum_{i=1}^{N} \nabla_{\chi_i}^2 + \frac{1}{2}\sum_{i=1}^{N} \omega_i^2 \chi_i^2 + \sum_{i>j=1}^{N} \omega_i \omega_j \sqrt{\alpha_i \alpha_j}\, \boldsymbol{\chi}_i \mathcal{T}_{ij} \boldsymbol{\chi}_j .$$

$$E_{\mathrm{vdW}} = \frac{1}{2}\sum_{p=1}^{3N} \sqrt{\lambda_p} - \frac{3}{2}\sum_{p=1}^{N} \omega_p^{\mathrm{SCS}},$$

A. Tkatchenko, R. A. DiStasio Jr., R. Car, M. Scheffler, PRL (2012).

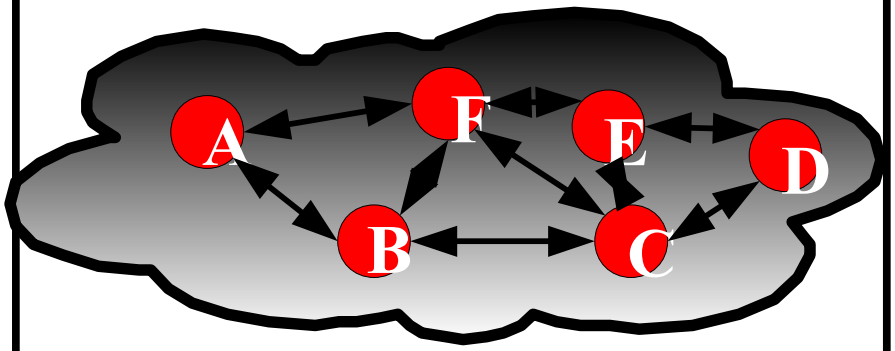
Many-body dispersion effects

The current state-of-the-art (*Grimme, Becke, Tkatchenko/Scheffler, Langreth/Lundqvist, ...*):
Effective screening and two-body energy



Valid for
small molecules ***or***
homogeneous dielectrics

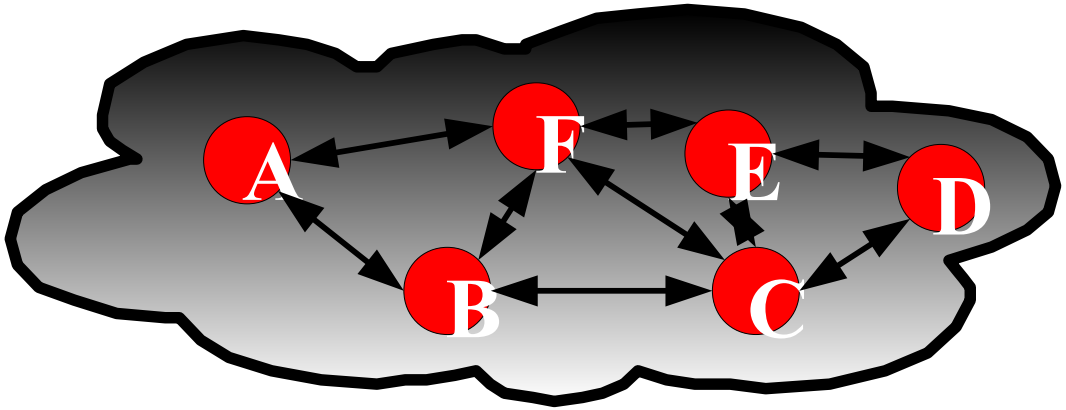
The new state-of-the-art:
Full many-body screening and energy for a system of quantum oscillators



Valid for **small and large molecules, insulators,** metals, interfaces, ...

Many-body dispersion effects

Important features of DFT+MBD



Seamless treatment of short-range (quantum) and long-range (classical) screening

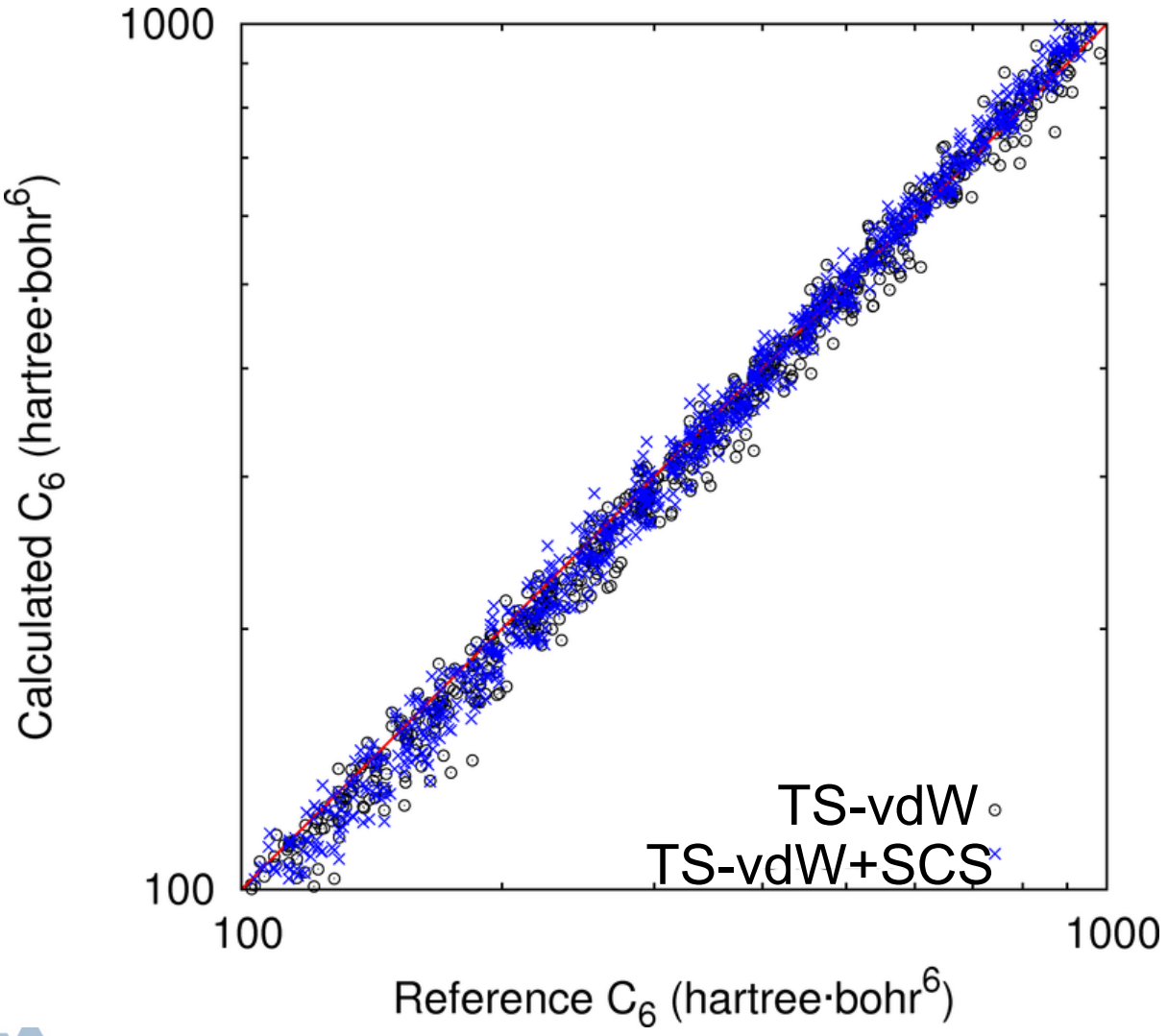
Models anisotropy, polarization, and depolarization for non-metallic molecules and solids

Computes many-body vdW energy to *infinite order* with a single parameter

Negligible computational cost compared to DFT (MBD calculation takes 1 min. for 1000 atoms on 1 processor)

Many-body dispersion effects

C_6 coefficients: **1225** atomic/molecular dimers

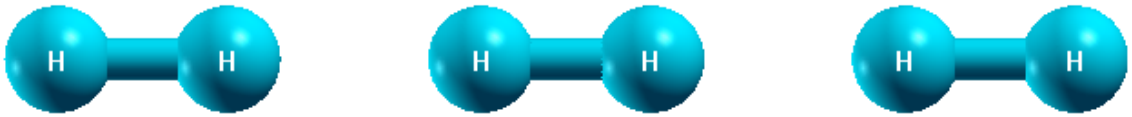


$$C_6^{AB} = \frac{3}{\pi} \int \alpha_A(i\omega)\alpha_B(i\omega)\,d\omega$$

A. Tkatchenko and M. Scheffler, ***PRL*** (2009)

Many-body dispersion effects

SCS: Polarization and anisotropy in H_6



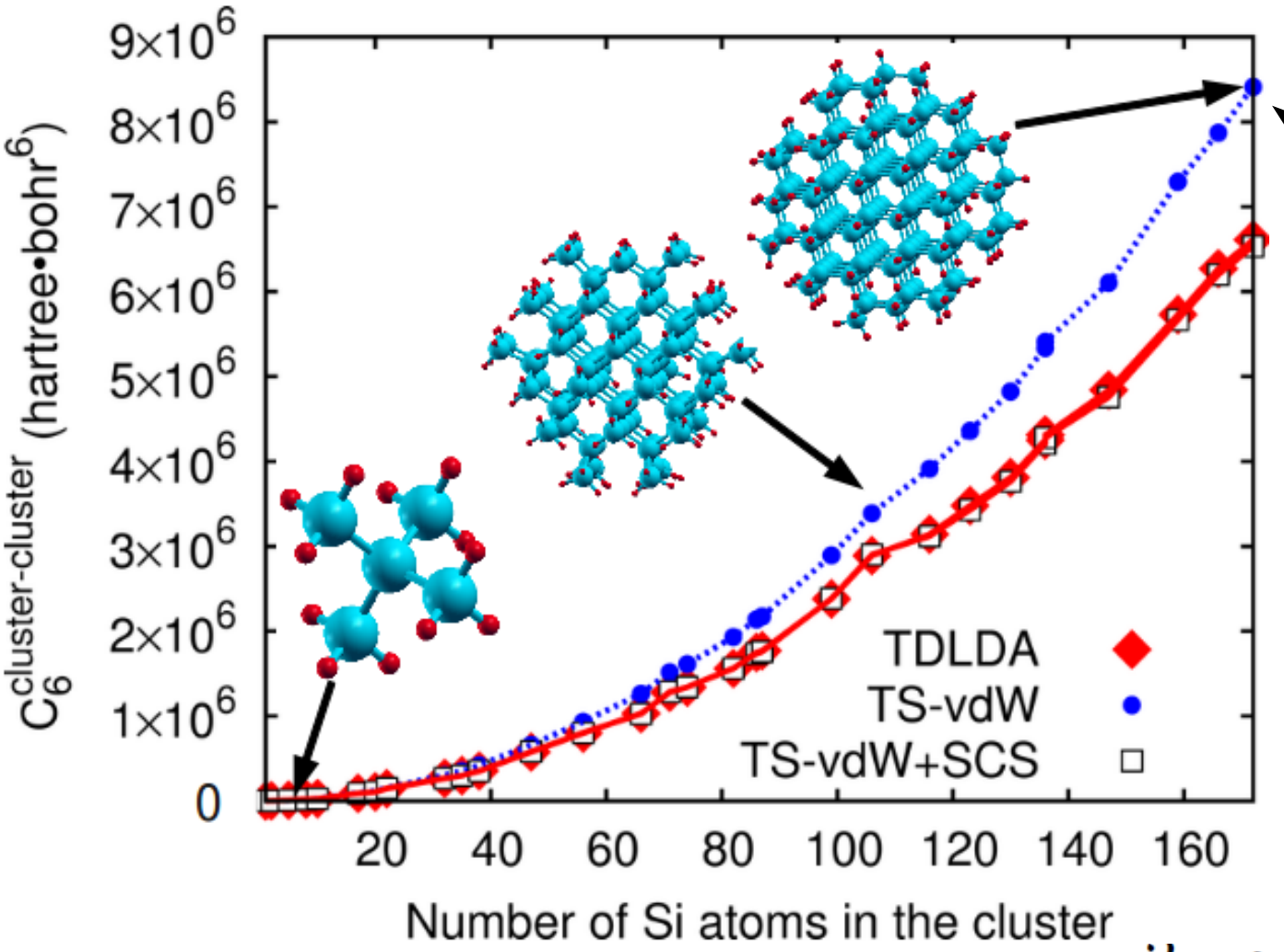
	$C_{6\perp}$	$C_{6\parallel}$	C_6^{iso}	
TS-vdW:	166	161	165	
+SCS:	89	692	223	
LR-CCSD:	115	638	238	(Reference)

$$C_6^{AA} = \frac{3}{\pi} \int [\alpha_A(i\omega)]^2 d\omega$$

All values in Hartree Bohr^6

Many-body dispersion effects

C_6 coefficients: from small to large silicon clusters

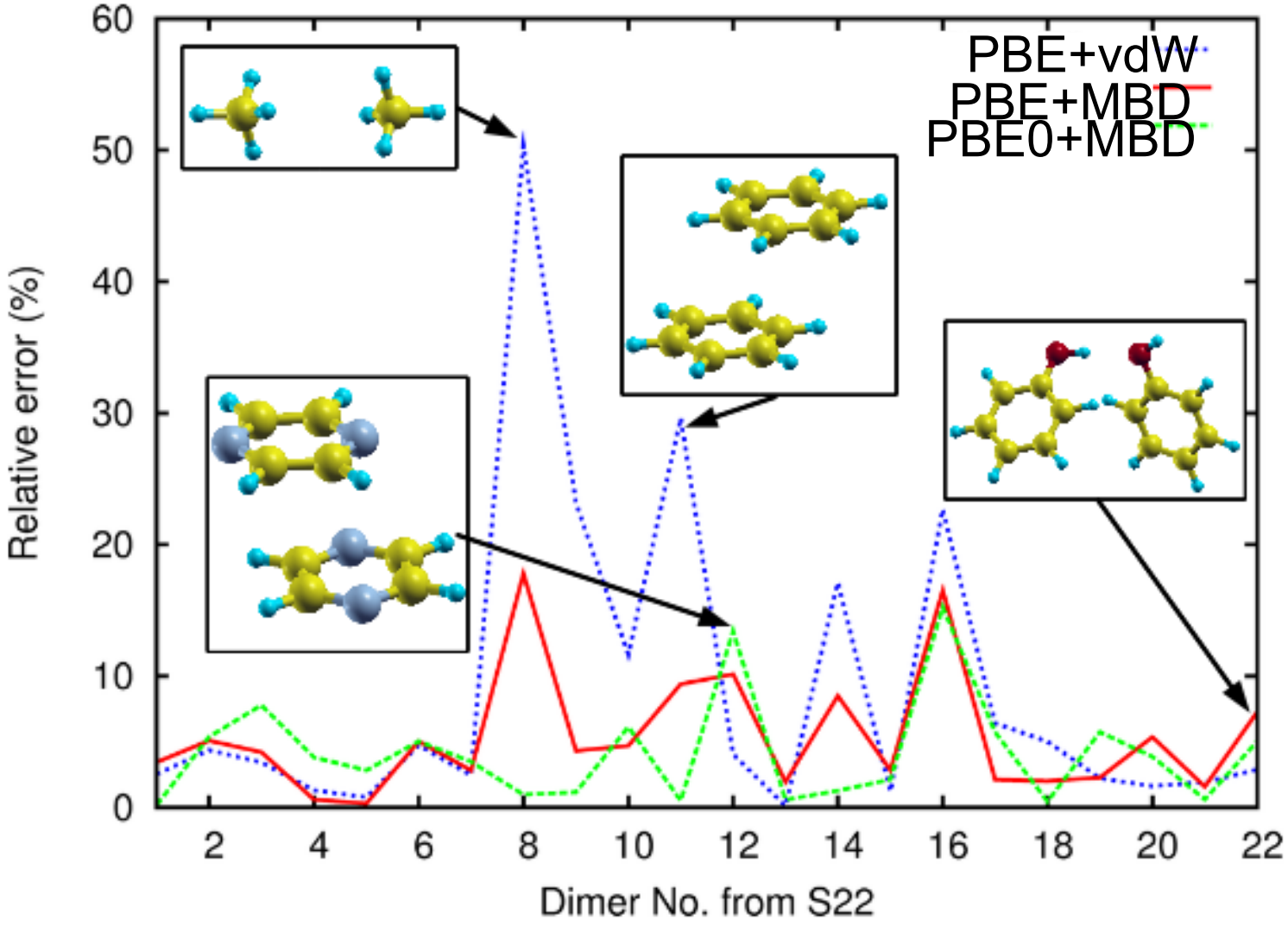


27% erro

$$C_6^{AA} = \frac{3}{\pi} \int [\alpha_A(i\omega)]^2 d\omega$$

TDLDA: *S. Botti et al.*, ***PRB*** (2008)

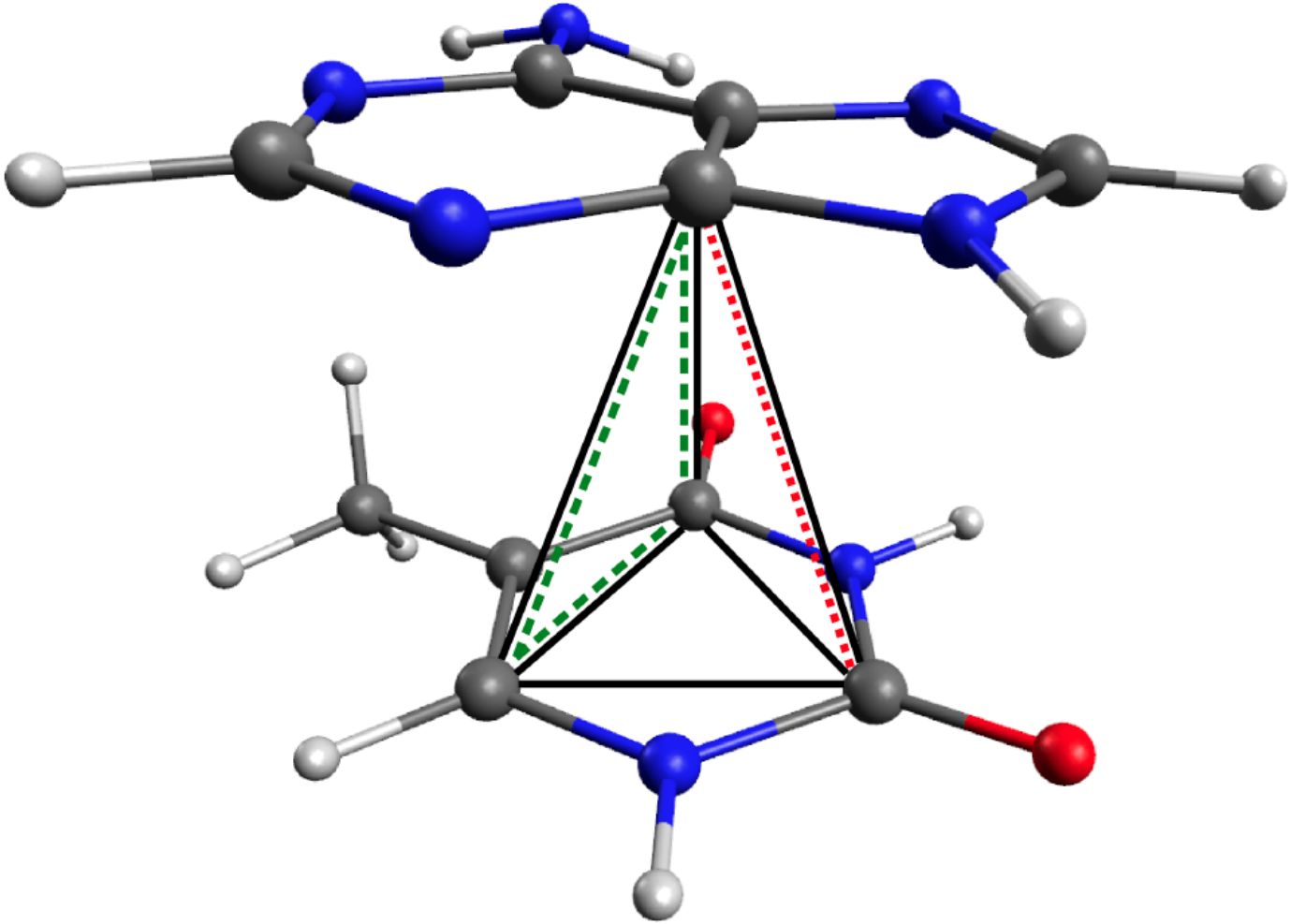
PBE(0)+MBD: S22 database



MARE
PBE+vdW
9.1%
PBE+MBD
5.4%
PBE0+MBD
4.2%

S22 CCSD(T): *Jurecka, Sponer, Cerny, Hobza,* ***PCCP*** (2006); *Scherrill et al.,*

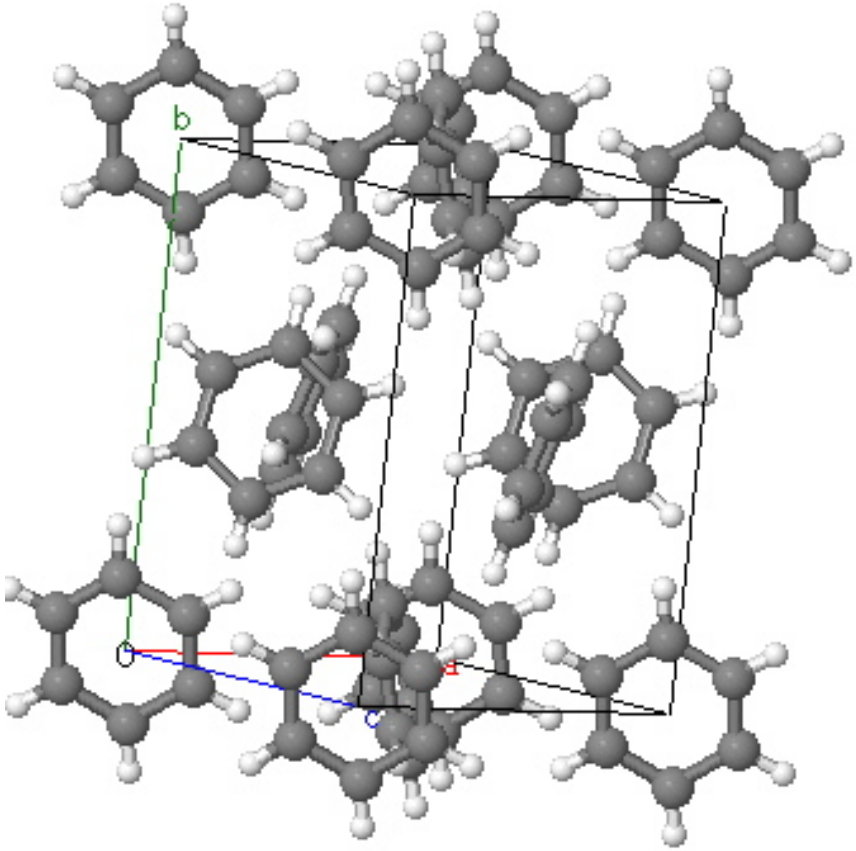
Many-body dispersion effects



Tkatchenko, von Lilienfeld, DiStasio, submitted to PNAS (2012)

Many-body dispersion effects

Many-body vdW effects at play: Benzene molecular crystal



PBE+vdW
690 meV/molecule

PBE+MBD
565 meV/molecule

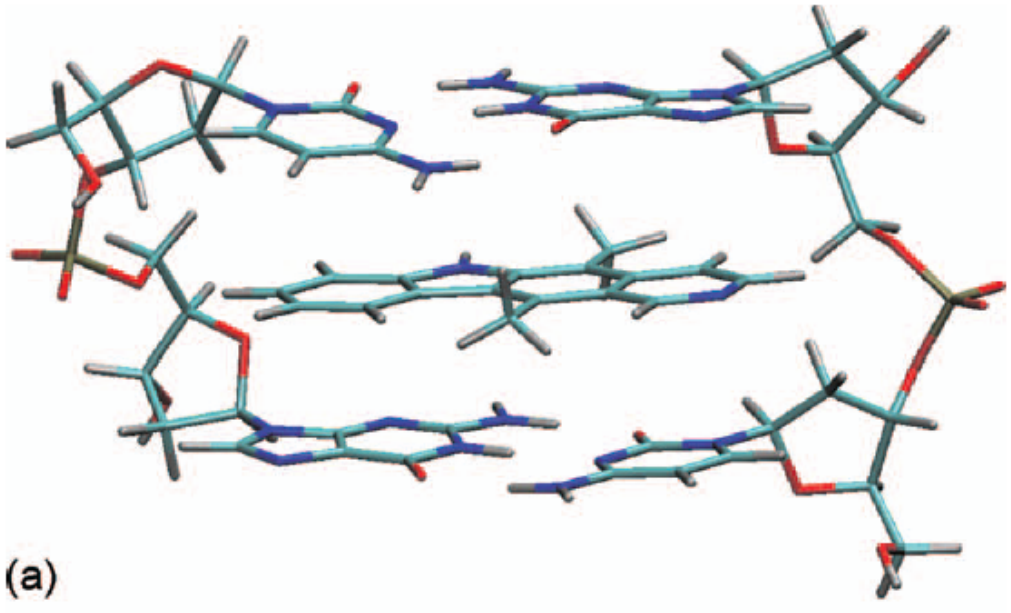
2.9 kcal/mol
due to screening
and many-body
VdW effects

Experiment
518-560 meV/molecule

Tkatchenko, von Lilienfeld, DiStasio, submitted to PNAS (2012)

Many-body dispersion effects

Many-body vdW effects at play: Ellipticine



BLYP+DCACP
-37 kcal/mol

PBE+vdW
-46.6 kcal/mol

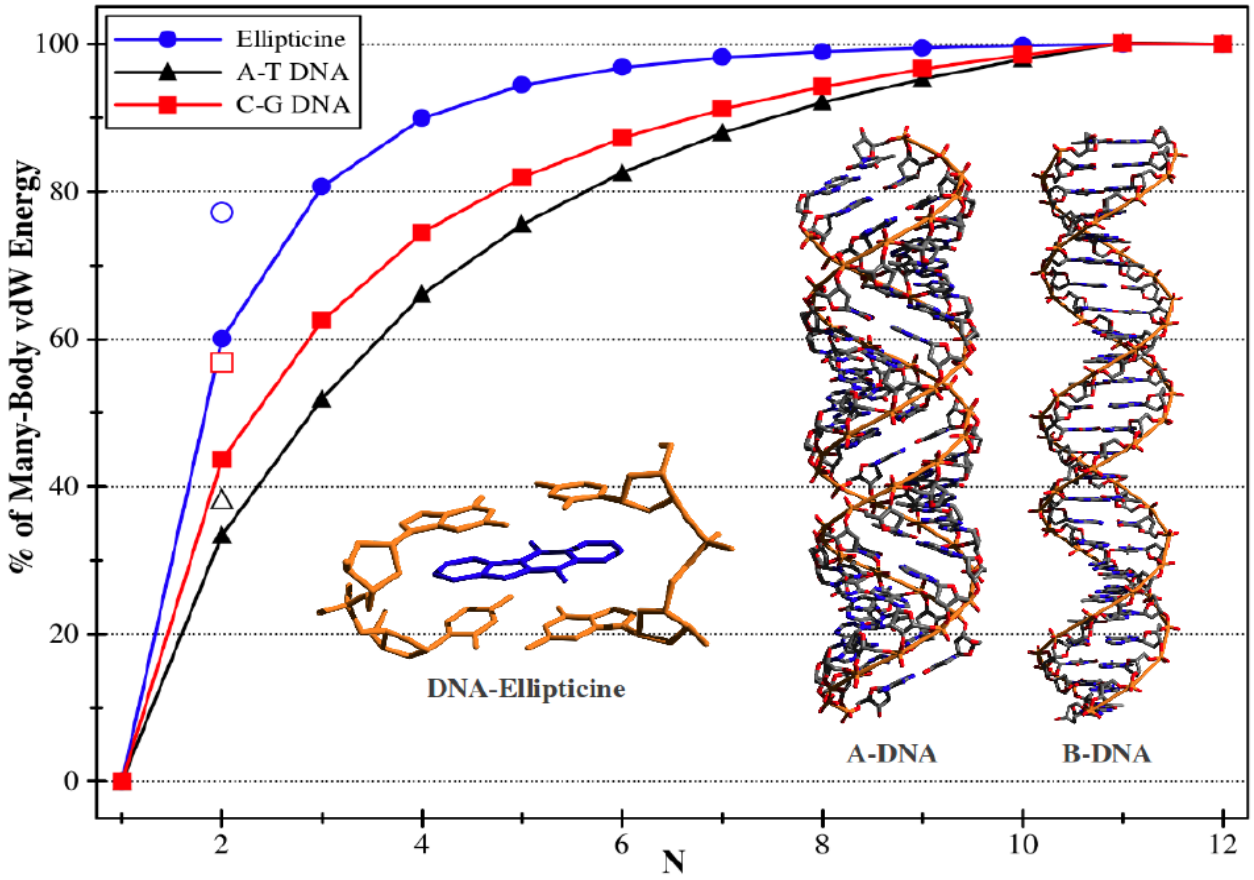
PBE+MBD
-55.0 kcal/mol

Lin, von Lilienfeld, Coutinho-Neto, Tavernelli, Rothlisberger, ***J. Phys. Chem. B*** (2007); *von Lilienfeld and Tkatchenko*, ***J. Chem. Phys.*** (2010).

Tkatchenko, von Lilienfeld, DiStasio, submitted to PNAS (2012)

Many-body dispersion effects

Level of Theory	ΔE_{bind}	$\Delta E_{\mathrm{B-A}}^{\mathrm{A:T}}$	$\Delta E_{\mathrm{B-A}}^{\mathrm{C:G}}$
DFT	+5.2	+4.2	+1.9
vdW-MB(2)	-39.1	+2.6	-3.5
vdW-MB	-50.7	-0.1	-8.2



Tkatchenko, von Lilienfeld, DiStasio, submitted to PNAS (2012)

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Outlook

BG/Q

(Mira)

PETAFLOPS POWER

48 racks

1,024 nodes per rack

1.6 GHz 16-way core processor

16 GB RAM per node

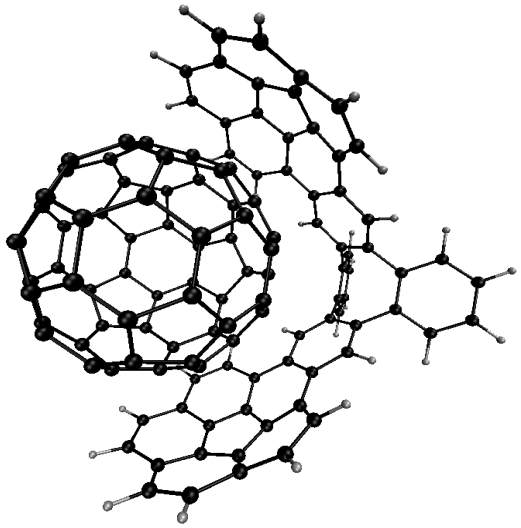
384 I/O nodes

240 GB/s, 35 PB storage

That's a total of 768K cores, 768 terabytes of RAM, and a peak performance of 10 petaflops.

The system is capable of carrying out 10 quadrillion floating-point operations per second.

- Argonne Leadership Computing Facility promotes open science internationally through INCITE program (http://www.alcf.anl.gov/)
- Systems:
  - Large and crowded
  - Many
- Methods: High quality (QMC, MBPT, CCSD(T) ...)



Acknowledgments

Rothlisberger, EPFL

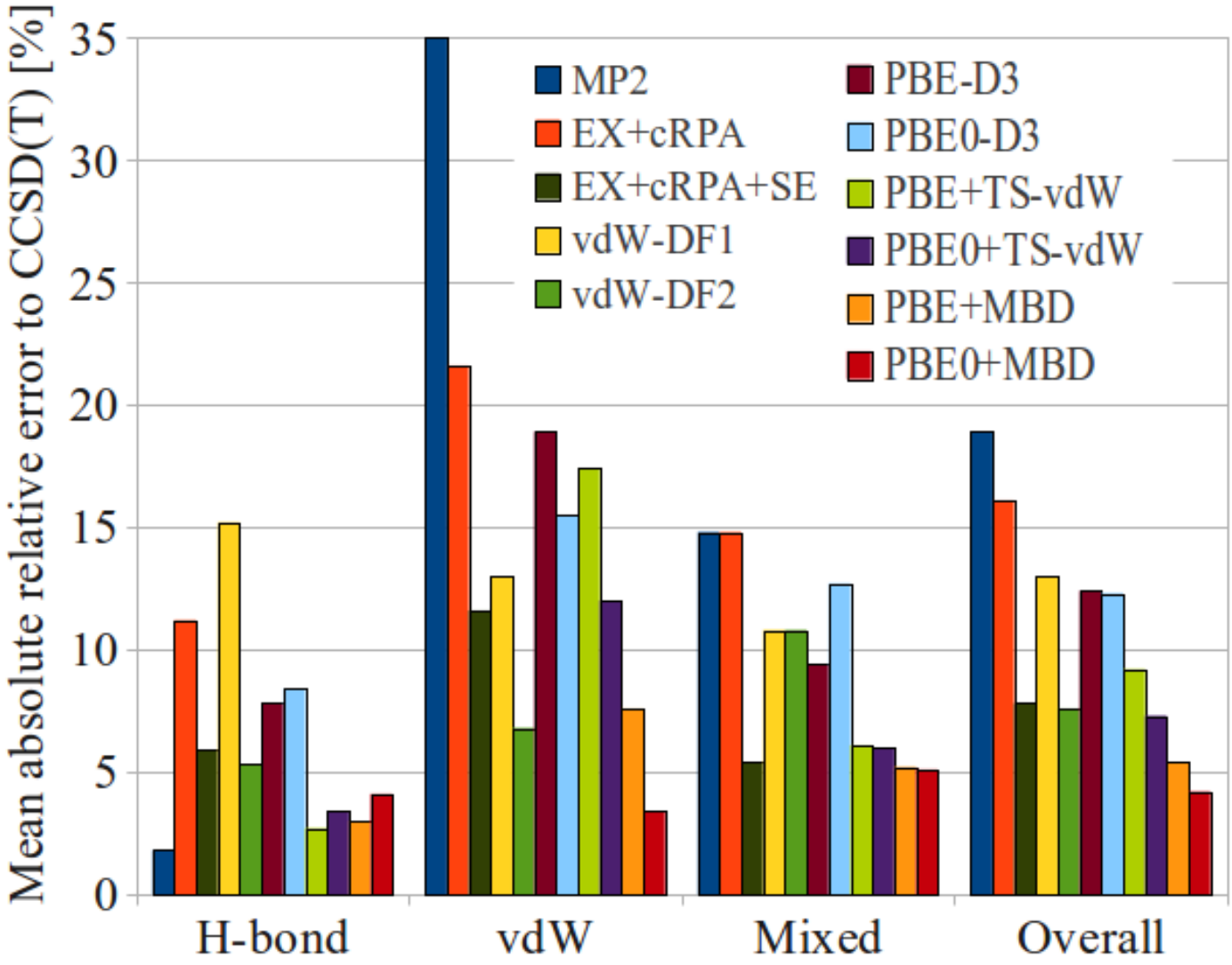
Tavernelli, EPFL

Sebastiani, FU Berlin

Tkatchenko, FHI Berlin

DiStasio, Princeton

S22 database: Comparison with other approaches



S22 CCSD(T): *Jurecka, Sponer, Cerny, Hobza,* ***PCCP*** (2006); *Scherrill et al.,* ***JCP*** (2010).