



MAX-PLANCK-GESELLSCHAFT



Practical Approaches to van der Waals Interactions

Alexandre Tkatchenko

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Berlin, Germany*

ICTP, Trieste, Aug 13, 2013



MAX-PLANCK-GESELLSCHAFT



Practical Approaches to van der Waals Interactions

or

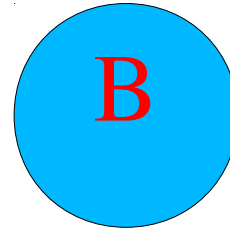
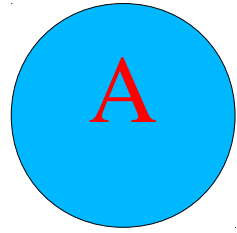
When $(2 + 2) \neq 4$?

Alexandre Tkatchenko

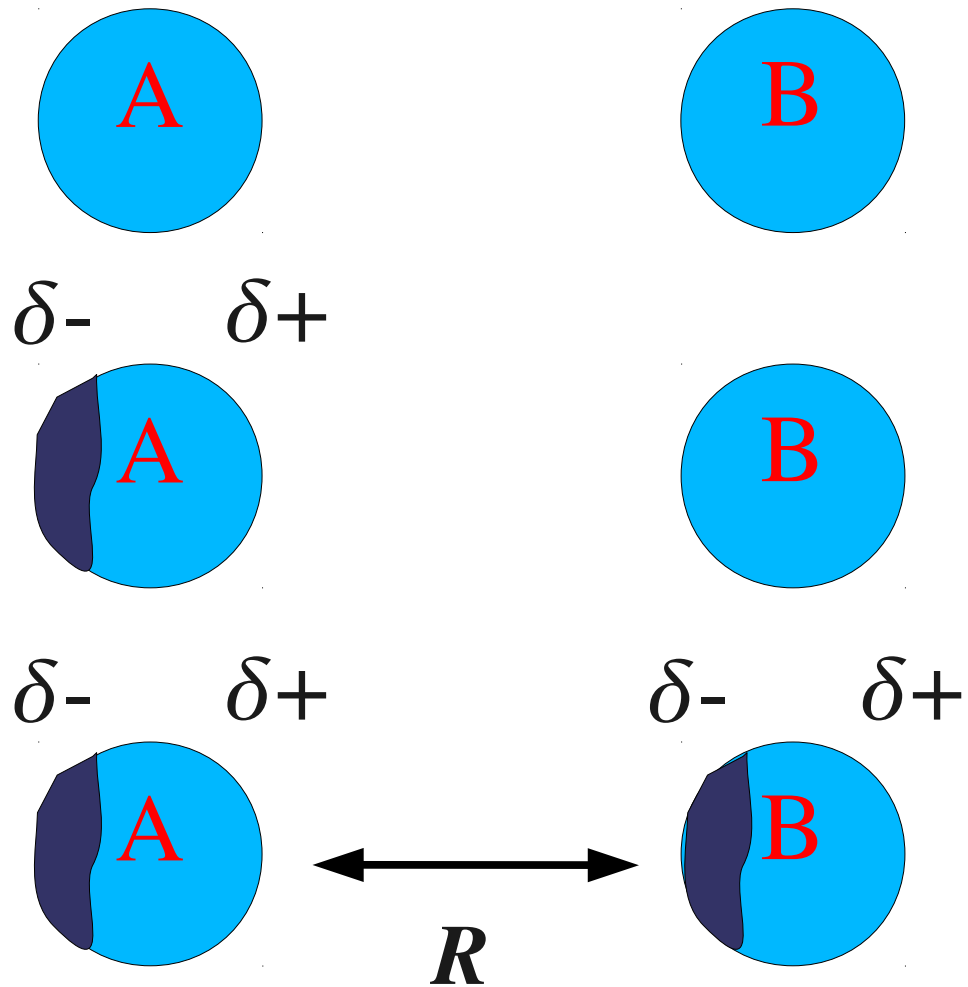
*Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Berlin, Germany*

ICTP, Trieste, Aug 13, 2013

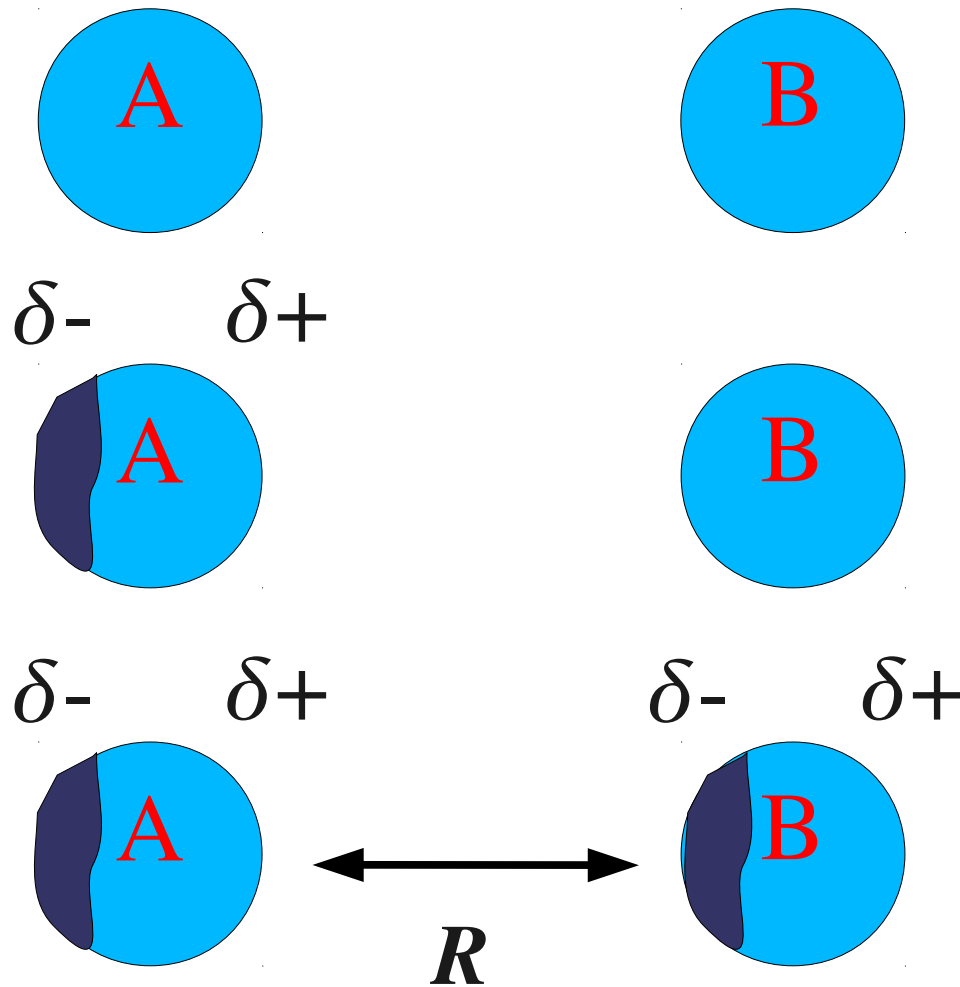
Textbook picture of vdW interactions



Textbook picture of vdW interactions

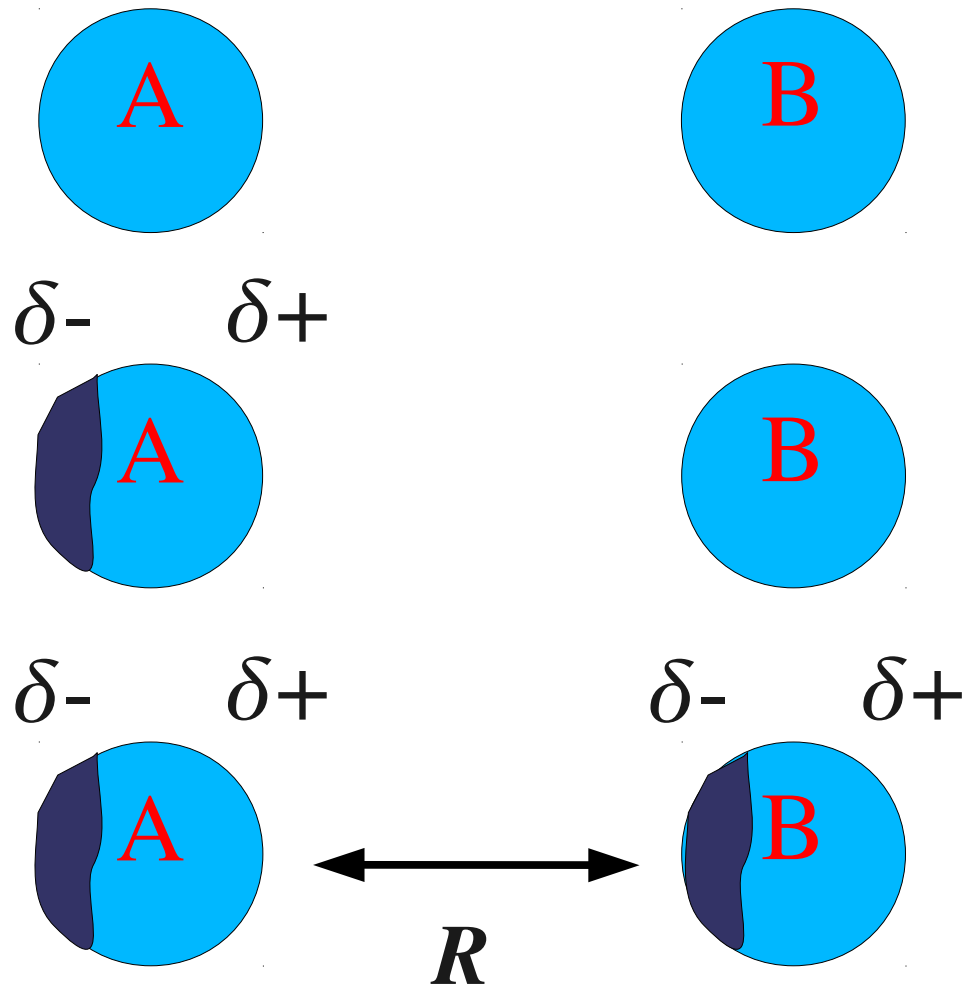


Textbook picture of vdW interactions



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

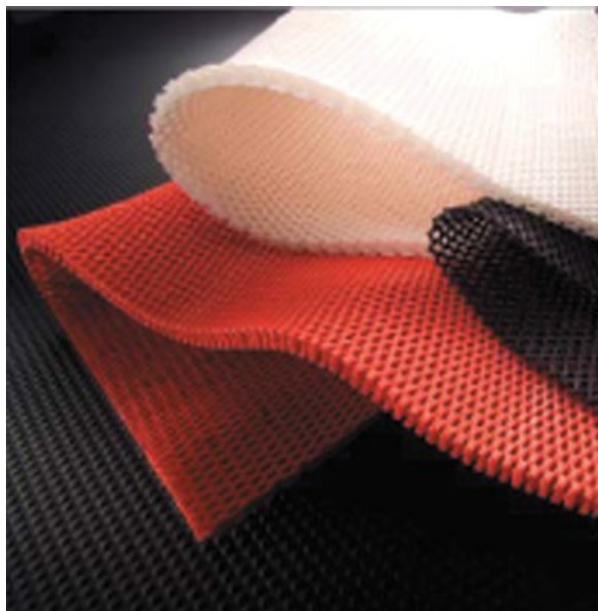
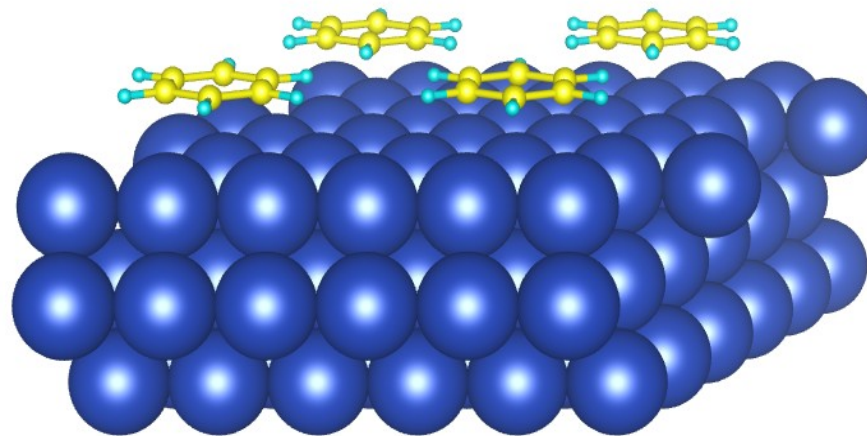
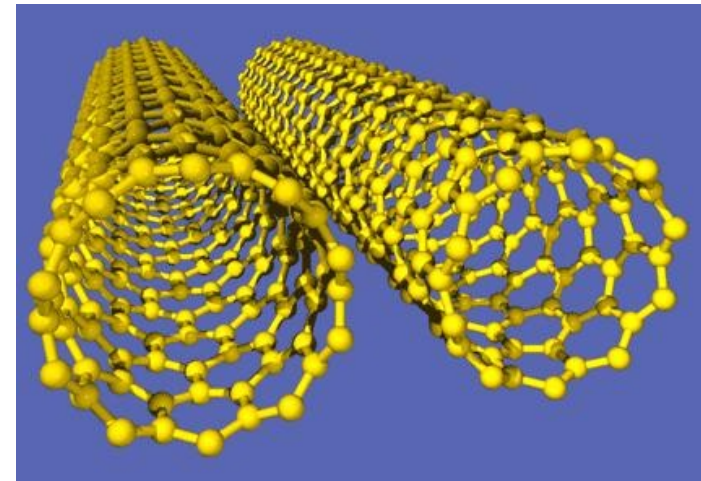
Textbook picture of vdW interactions



- **Ubiquitous** interatomic and intermolecular interaction
- Scales linearly with system size
- ... **and** it is a significant component of *binding energies* in large systems!

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

VdW Interactions in Soft and Hard Matter



Reality check for vdW from experiment

Selected for a **Viewpoint** in *Physics*
PHYSICAL REVIEW LETTERS

week ending
28 JUNE 2013

PRL 110, 263201 (2013)



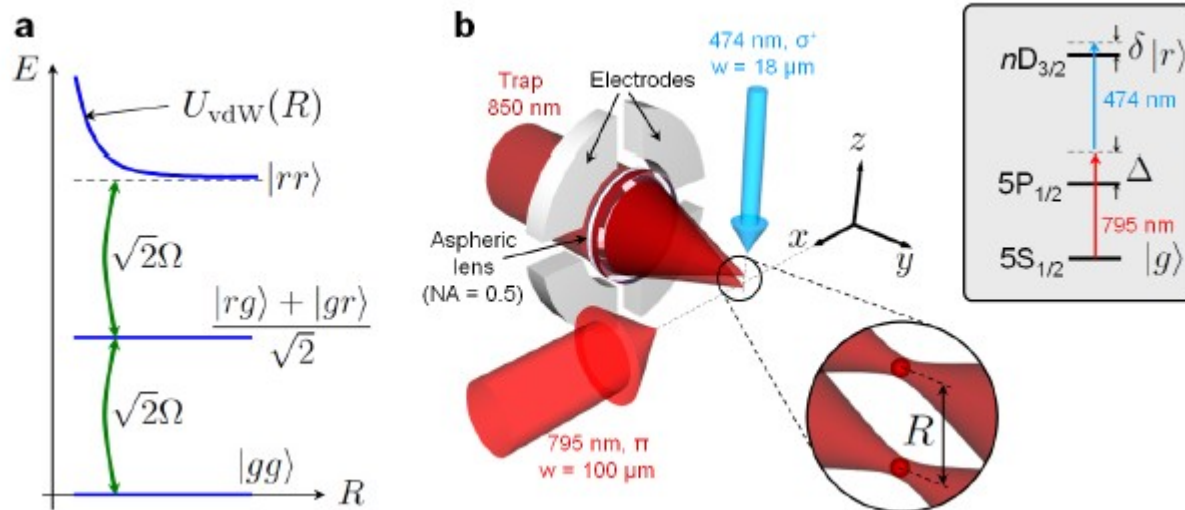
Direct Measurement of the van der Waals Interaction between Two Rydberg Atoms

L. Béguin,¹ A. Vernier,¹ R. Chicireanu,² T. Lahaye,¹ and A. Browaeys¹

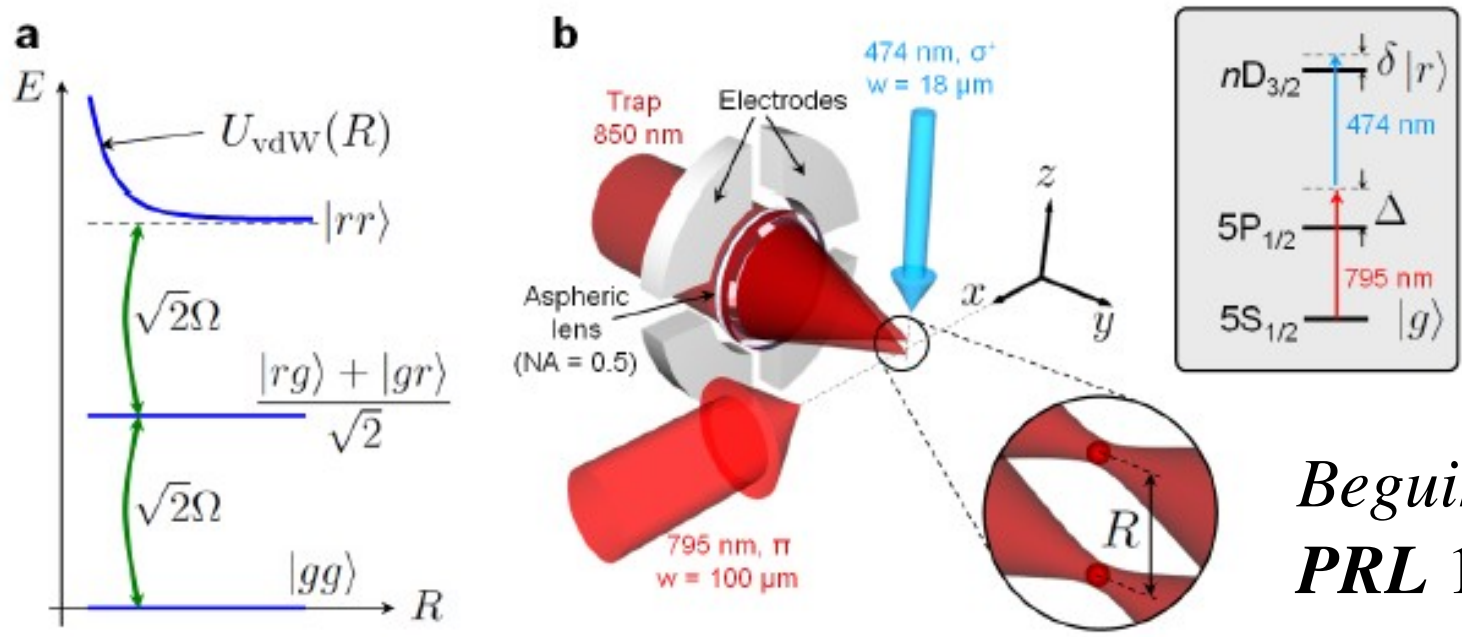
¹Laboratoire Charles Fabry, Institut d'Optique, CNRS, Univ Paris Sud, 2 avenue Augustin Fresnel, 91127 Palaiseau cedex, France

²Laboratoire de Physique des Lasers, Atomes et Molécules, Université Lille 1, CNRS; 59655 Villeneuve d'Ascq cedex, France

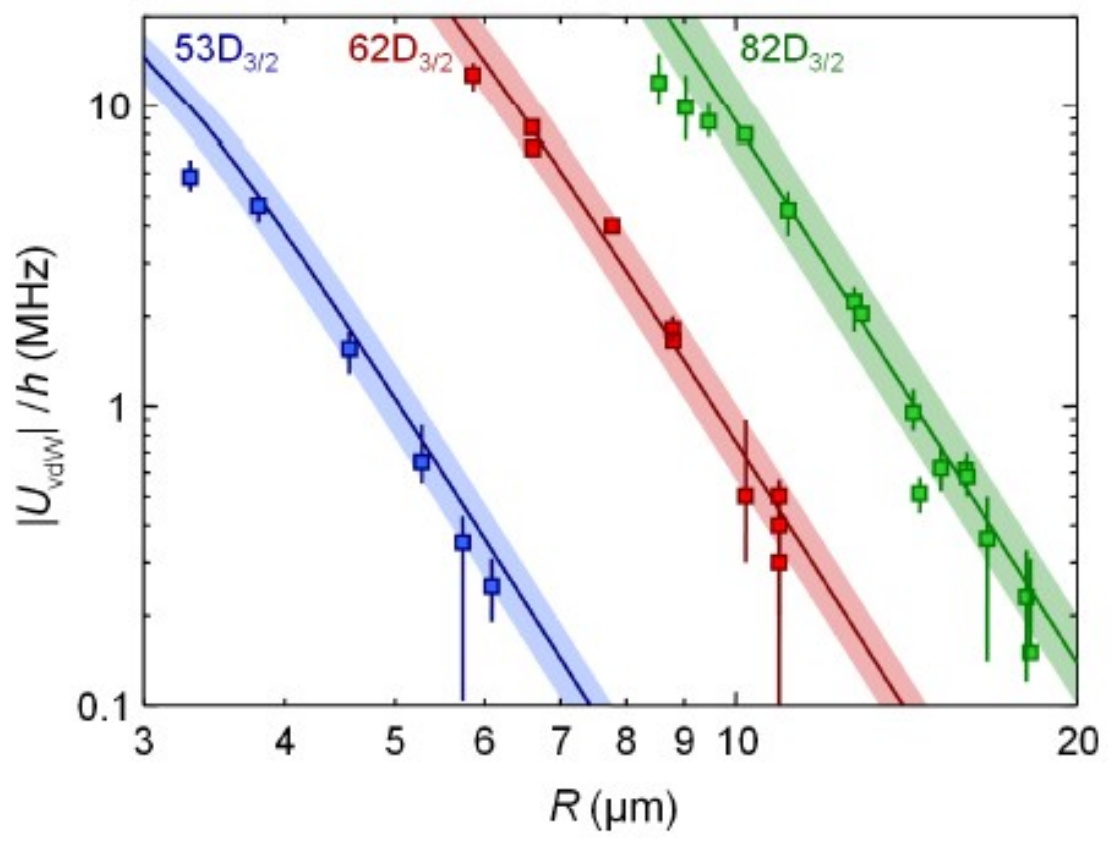
(Received 22 March 2013; published 24 June 2013)



Béguin et al.
PRL 110, 263201 (2013).

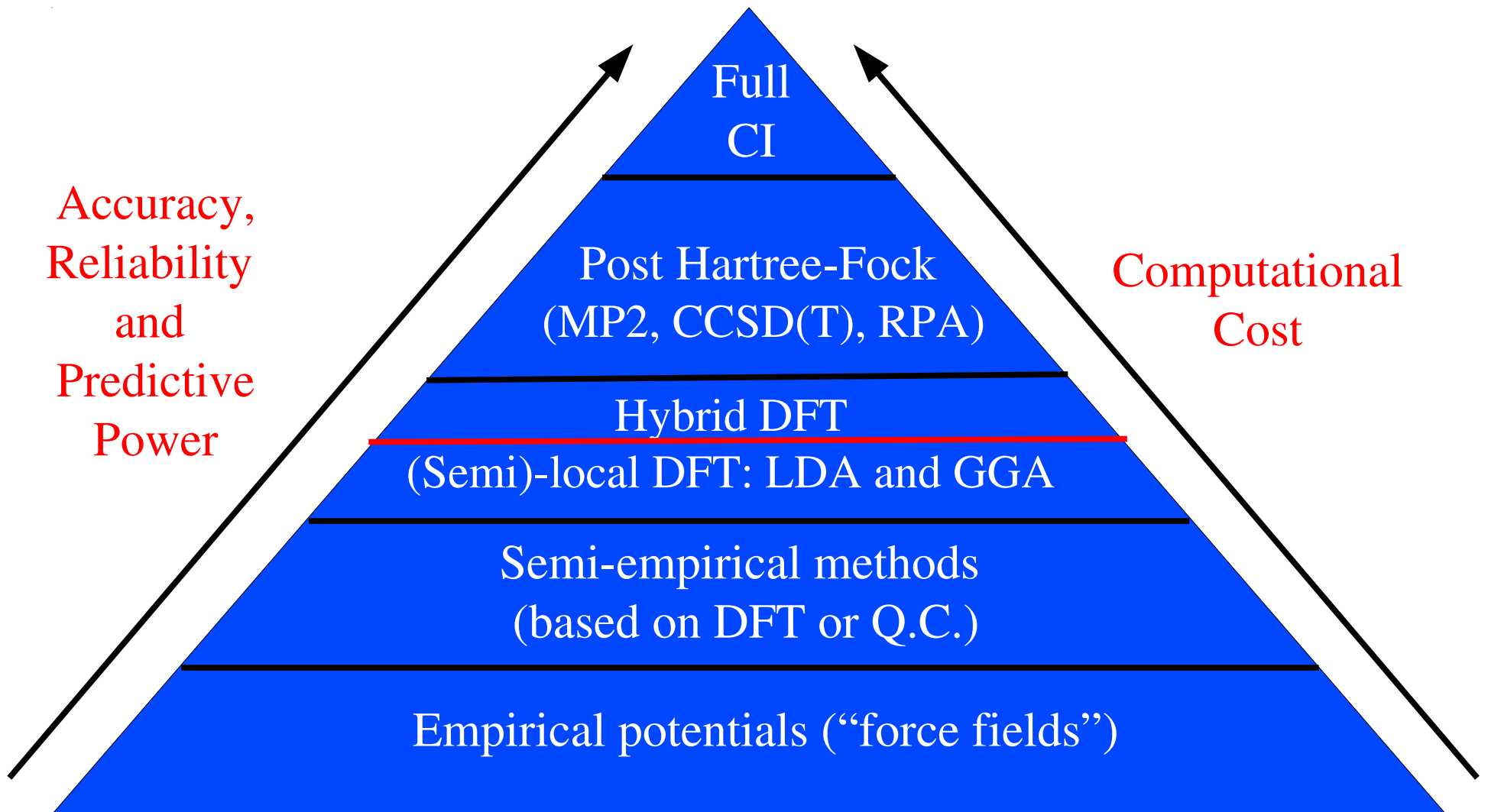


Beguin et al.
PRL 110, 263201 (2013).



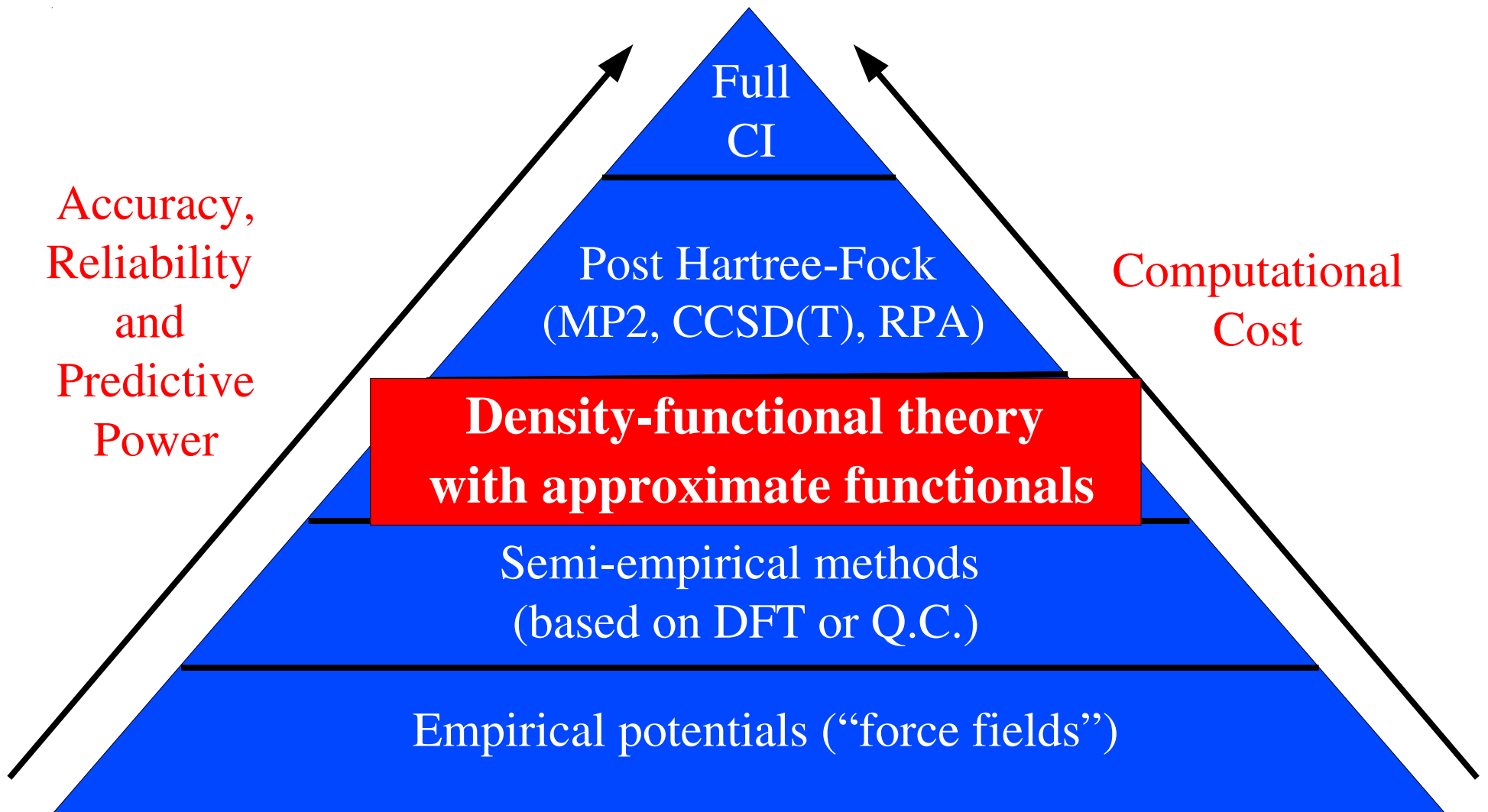
Current state-of-the-art of modeling

$$H\Psi = E\Psi$$



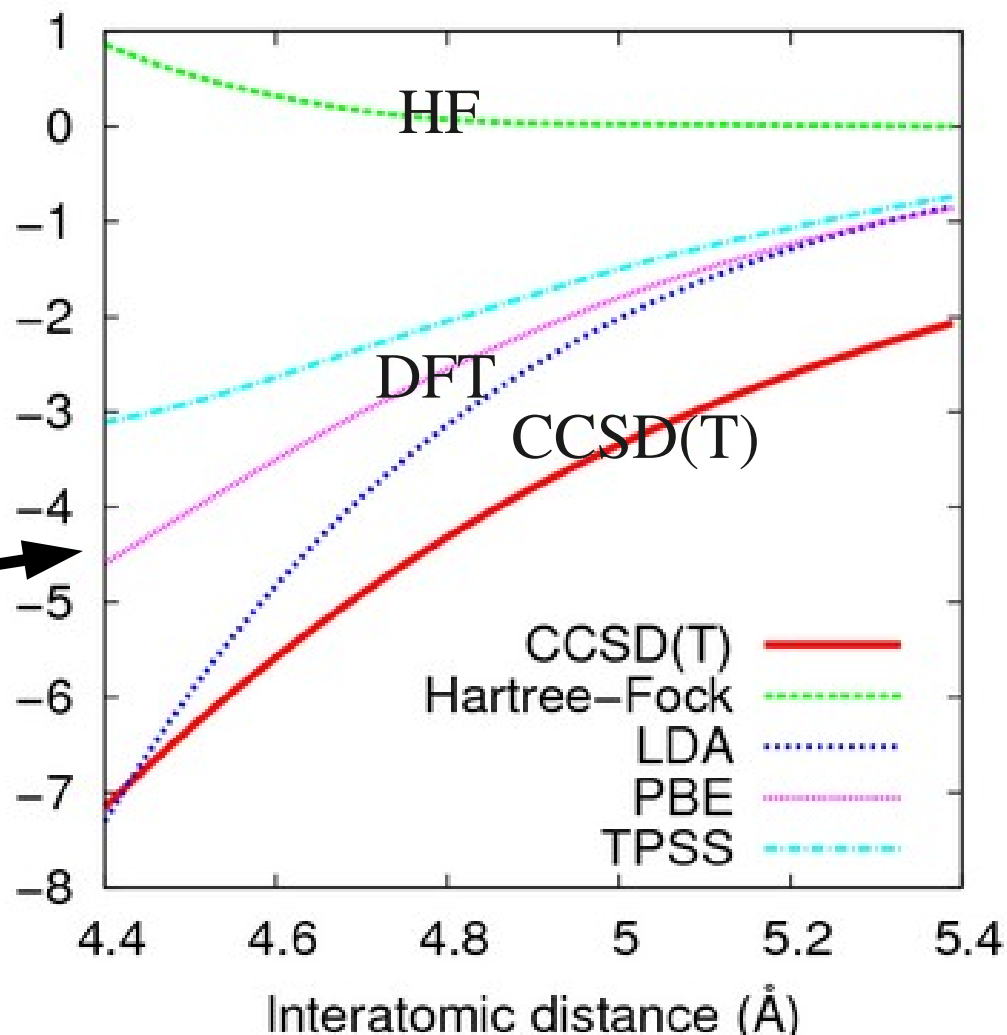
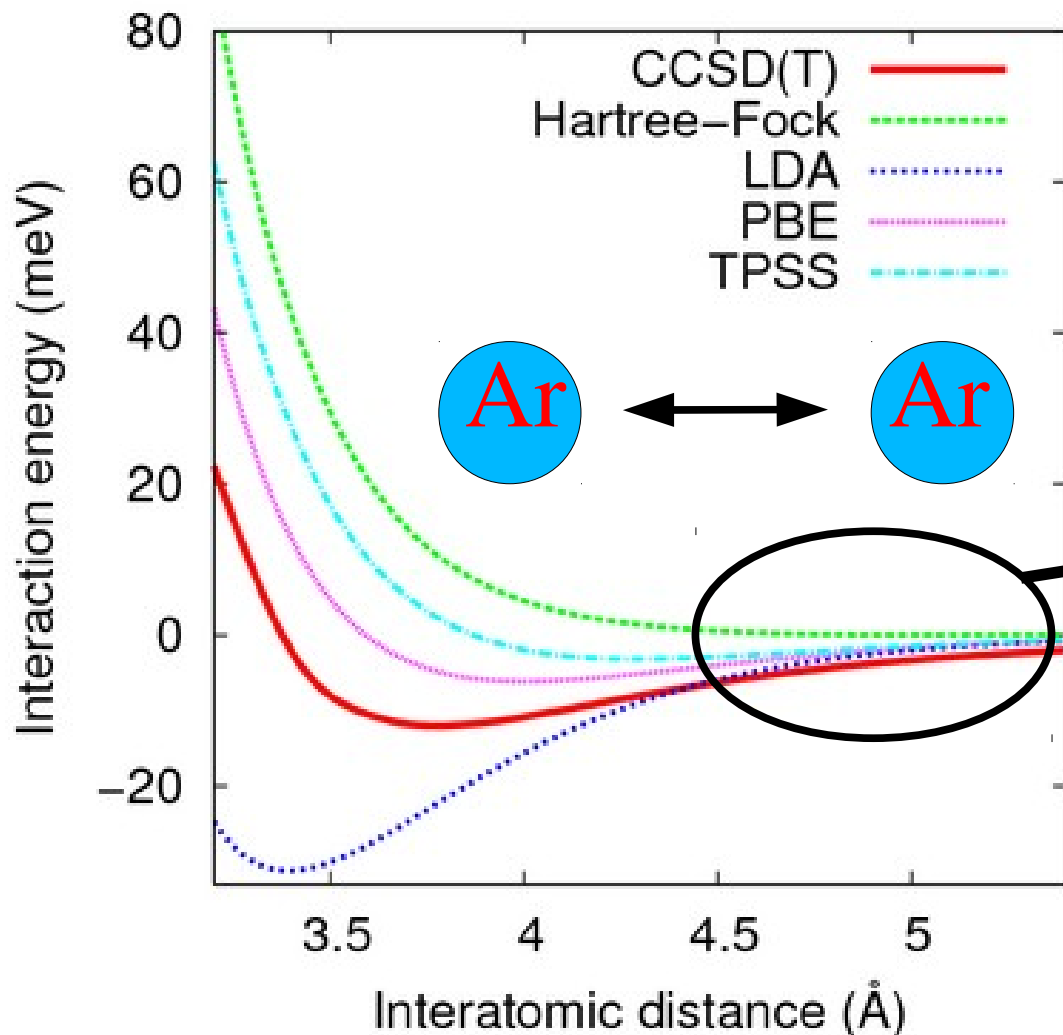
Current state-of-the-art of modeling

$$H\Psi = E\Psi$$



DFT and vdW interaction: Rare-gas dimers

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



(Approximate)
VdW-inclusive DFT methods

Review:

J. Klimes and A. Michaelides, J. Chem. Phys. 137, 120901 (2012)

Concepts and methods for dispersion in DFT

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

Concepts and methods for dispersion in DFT

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

- Non-local functionals (depend explicitly on \mathbf{r} and \mathbf{r}') (*Langreth, Lundqvist et al.*).
- Modified pseudopotentials (*von Lilienfeld et al.*)
- Highly empirical (hybrid) meta-GGA functionals (*Truhlar et al.*)
- Interatomic (pairwise or beyond) dispersion corrections (Many people)

Wu and Yang JCP (2002); Grimme J. Comp. Chem. (2004,2006); Dion et al. PRL (2004); Zhao and Truhlar JCP (2006); von Lilienfeld et al. PRL (2004); Johnson and Becke JCP (2005-2007); Tkatchenko and Scheffler PRL (2009); and many others ...

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

Langreth-Lundqvist functional

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

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

*Dion, Rydberg, Schroeder, Langreth, Lundqvist, **PRL** (2004).*

*Lee, Murray, Kong, Lundqvist, Langreth, **PRB** (2010).*

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

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

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

vdW-DF-04

- Exchange: revPBE
- Local corr.: LDA
- No free parameters
- C_6 error: $\sim 20\%$

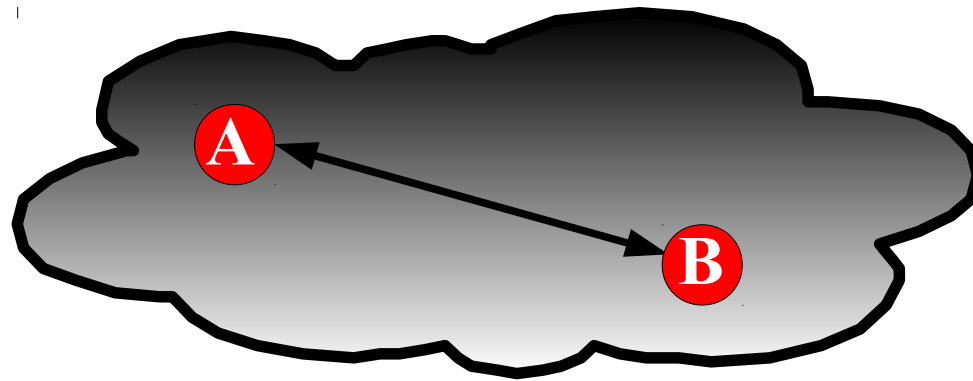
vdW-DF-10

- Exchange: PW86
- Local corr.: LDA
- 2 parameters
- C_6 error: $\sim 40\%$ ^(*)

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

Approximations for $E_{\text{corr}}^{\text{non-local}}$ in vdW-DF functional

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



- 1) Local approximation for the response function
- 2) Only pairwise point-point interaction, not including non-additive many-body vdW energy

See *J. F. Dobson and T. Gould, J. Phys. Condens. Matter* 24, 073201 (2012).

Interatomic vdW correction methods

Interatomic vdW methods

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

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

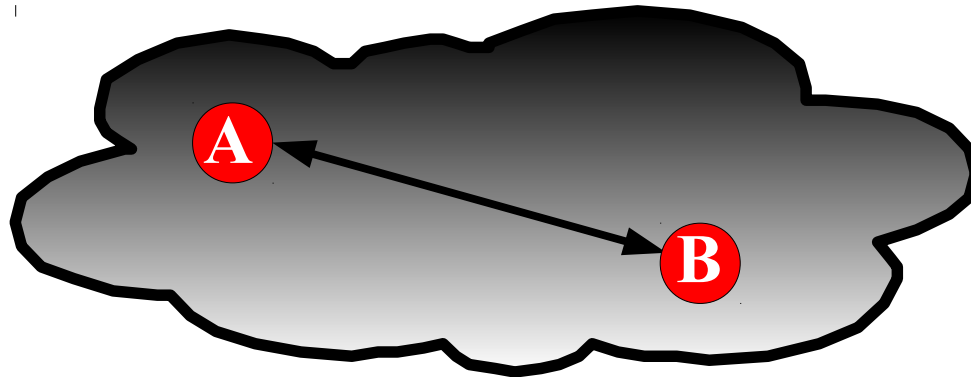
- Two parameters per atomic pair: (1) **VdW C_6 interaction coefficient** and (2) **vdW radius**.
- Clearly, if (1) and (2) are empirical, this leads to many fitting parameters. This was frequently the case before **2008**.

Evolution of interatomic vdW methods

- [Grimme's D1,D2 \(2004-2006\)](#): Parameterization for many elements in the periodic table
 - Highly empirical, some very *ad hoc* approximations
- [Jurečka *et al.* \(2007\)](#): Accurate parameterization for organic molecules
 - Better theoretical ground, but still very empirical
- [Johnson and Becke \(2005-2008\)](#), [Silvestrelli \(2008\)](#): C_6 and vdW radii from HF or DFT orbitals
 - Reduced empiricism, errors of $\sim 20\%$ - 40% in C_6 coefficients
- [Tkatchenko and Scheffler \(2009\)](#): C_6 coefficients and vdW radii from ground-state electron density
 - First-principles C_6 accurate to **5%**
-

What is missing in interatomic vdW corrections ?

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

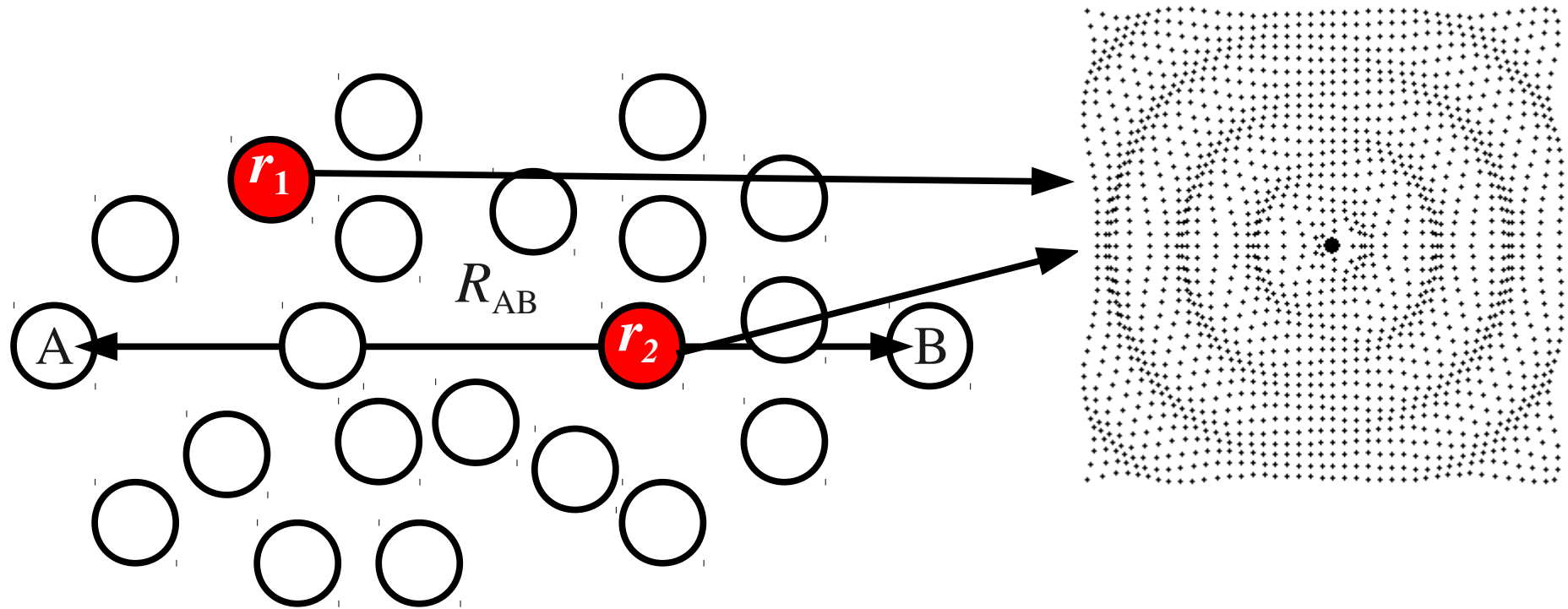


- 1) Long-range electrostatic screening among fluctuating dipoles
- 2) Non-additive many-body vdW energy beyond two-body

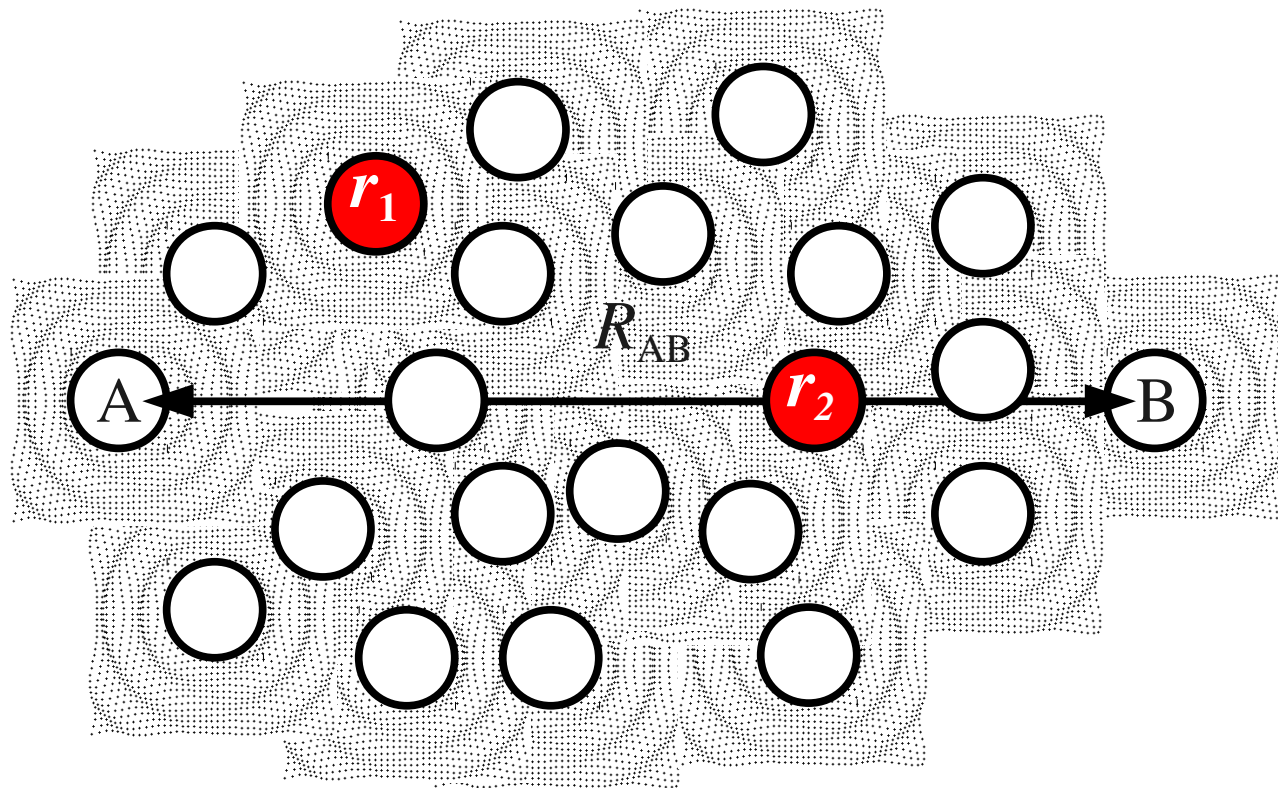
See A. Tkatchenko, A. Ambrosetti, R. A. DiStasio Jr.,
J. Chem. Phys. 138, 074106 (2013).

Beyond textbook picture of vdW interactions

Beyond textbook model of vdW interactions: Electrodynamic response effects



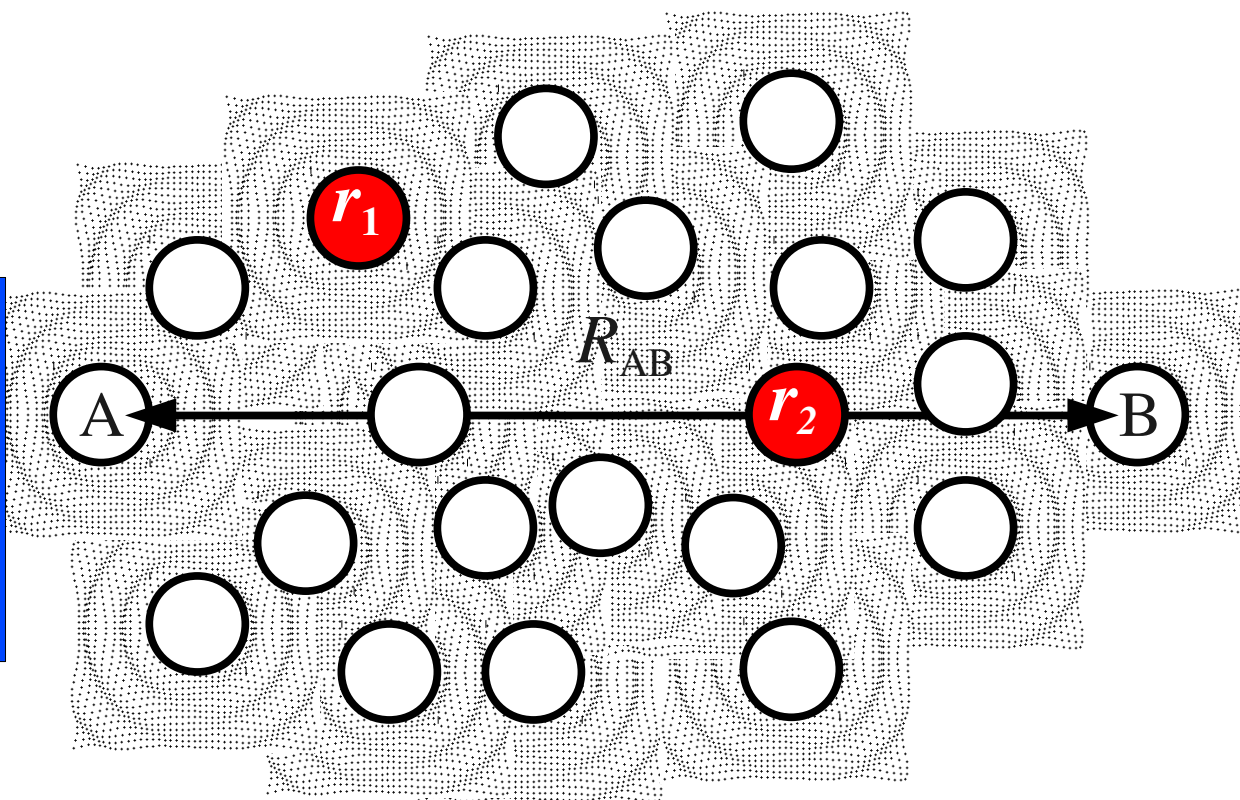
Beyond textbook model of vdW interactions: Electrodynamic response effects



Beyond textbook model of vdW interactions: Electrodynamic response effects

1

Accurate
Microscopic
Modeling of
Coulomb
Response



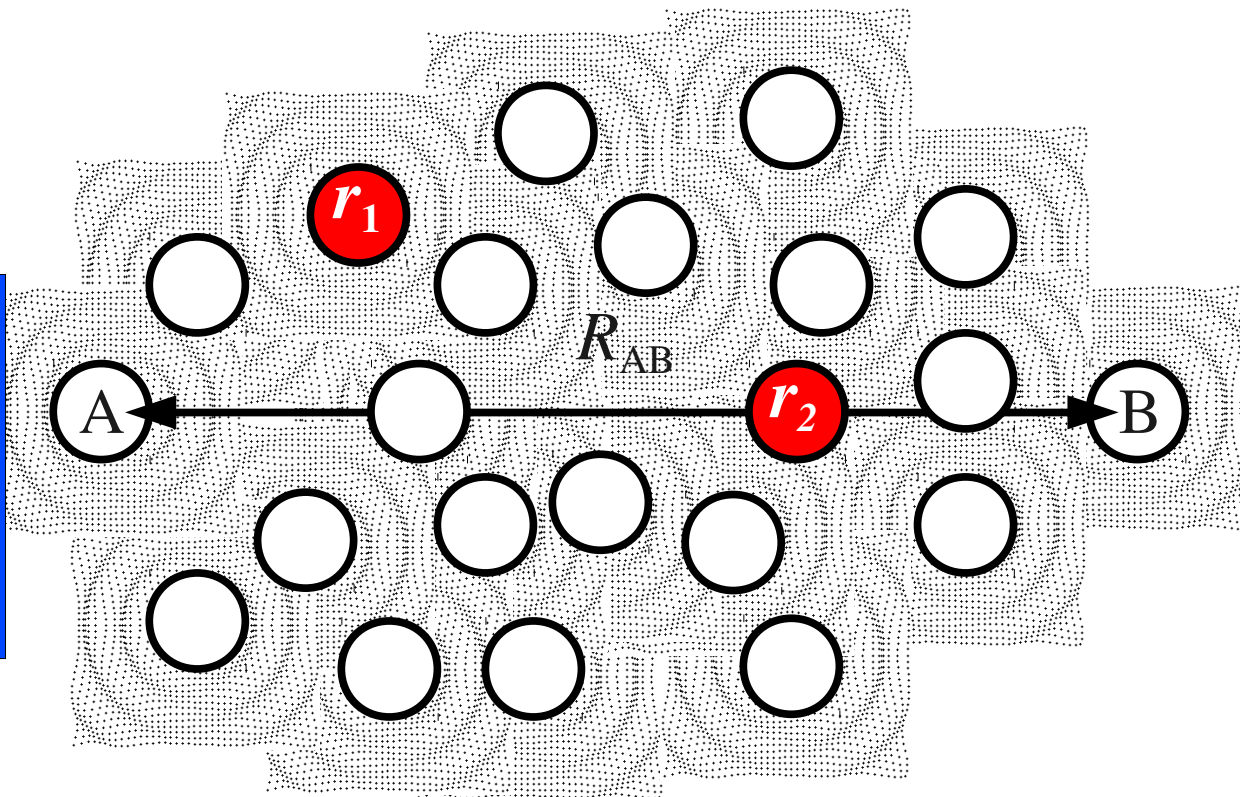
2

Full (All-Order)
Many-Body
van der Waals
Energy

Beyond textbook model of vdW interactions: Electrodynamic response effects

1

Accurate
Microscopic
Modeling of
Coulomb
Response



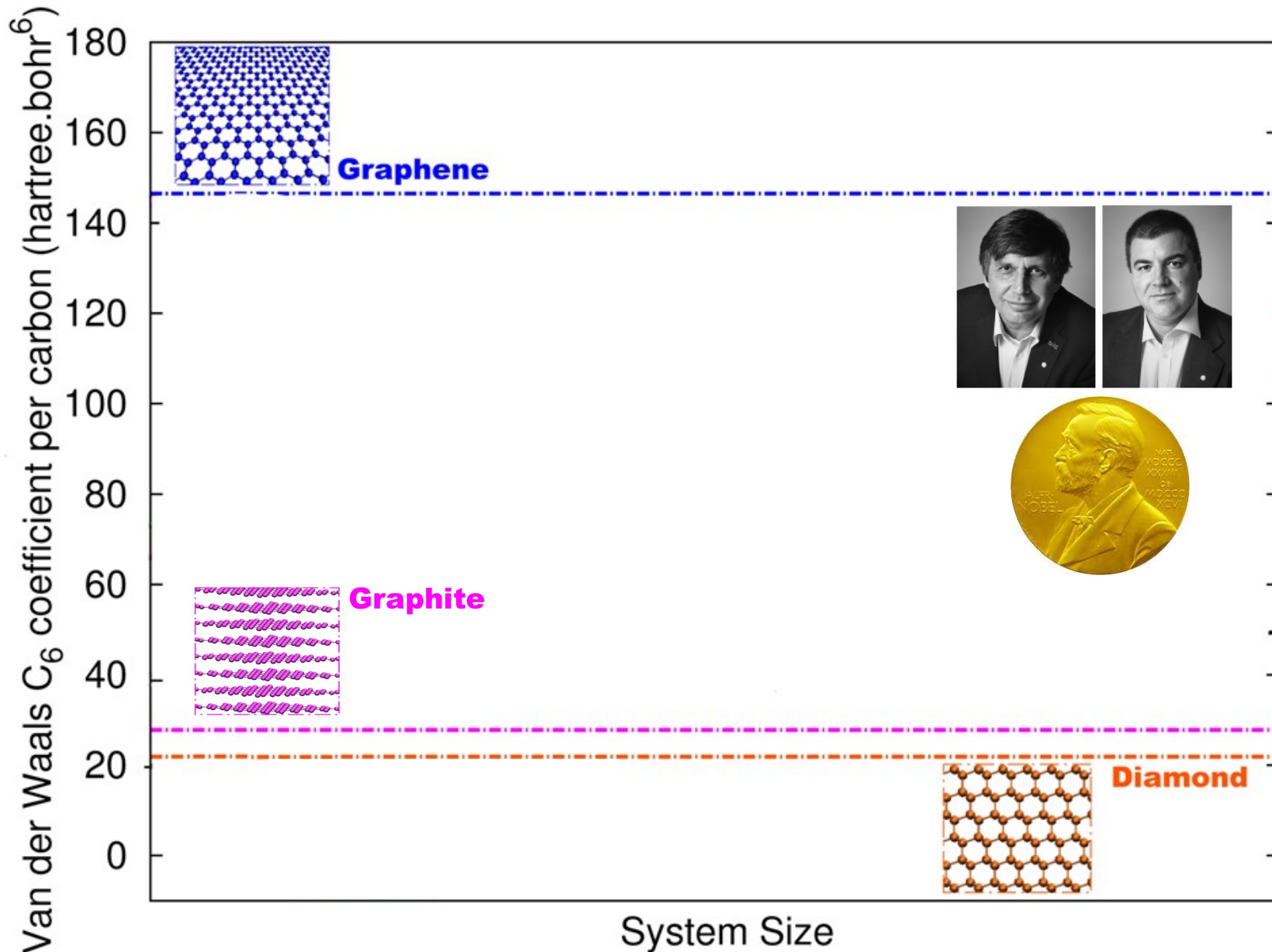
2

Full (All-Order)
Many-Body
van der Waals
Energy

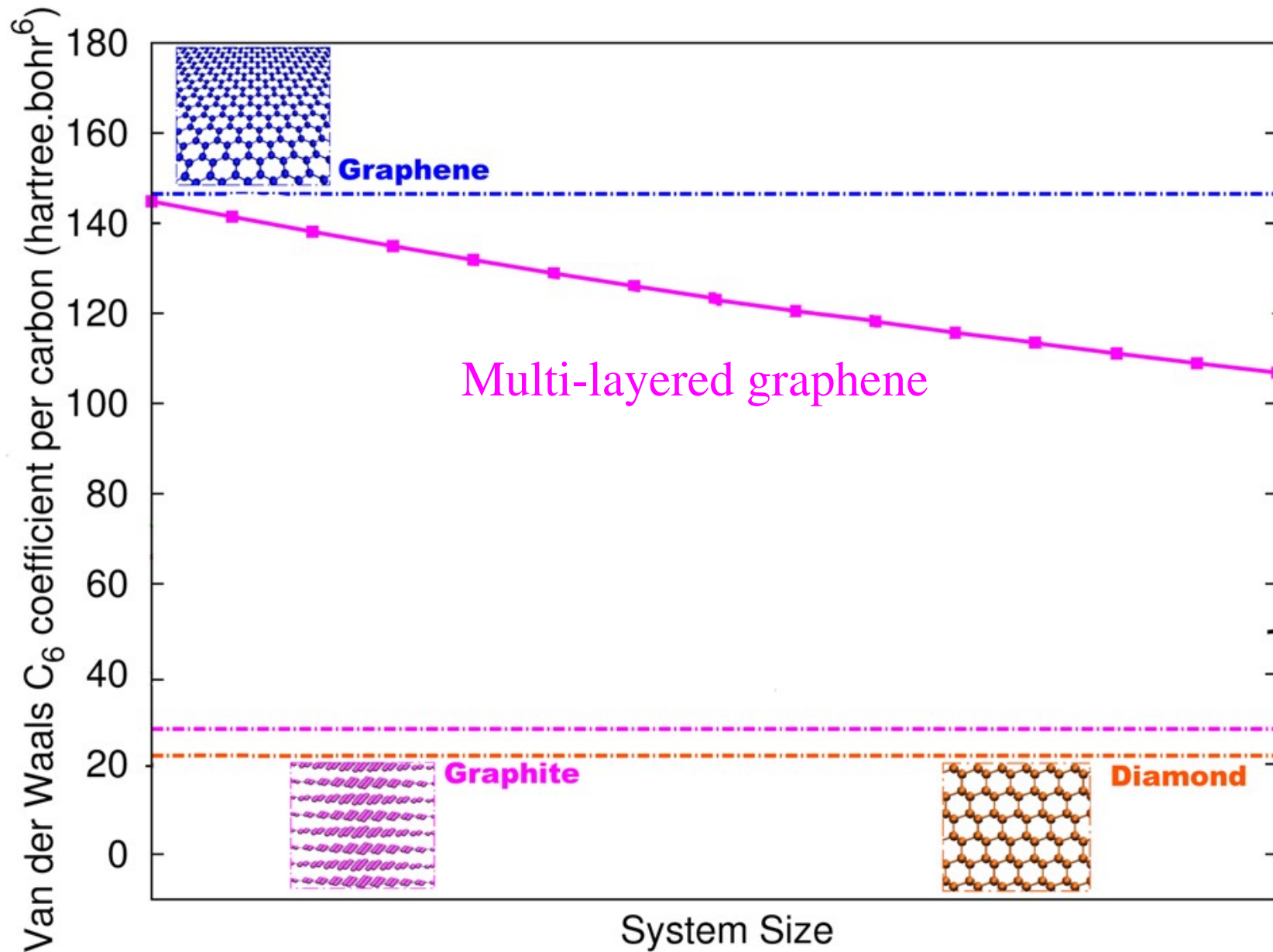
$$E_c = - \int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \text{Tr} \left((\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; i\omega) - \chi_0(\mathbf{r}_1, \mathbf{r}_2; i\omega)) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

We know how to solve the problem, albeit not very efficiently

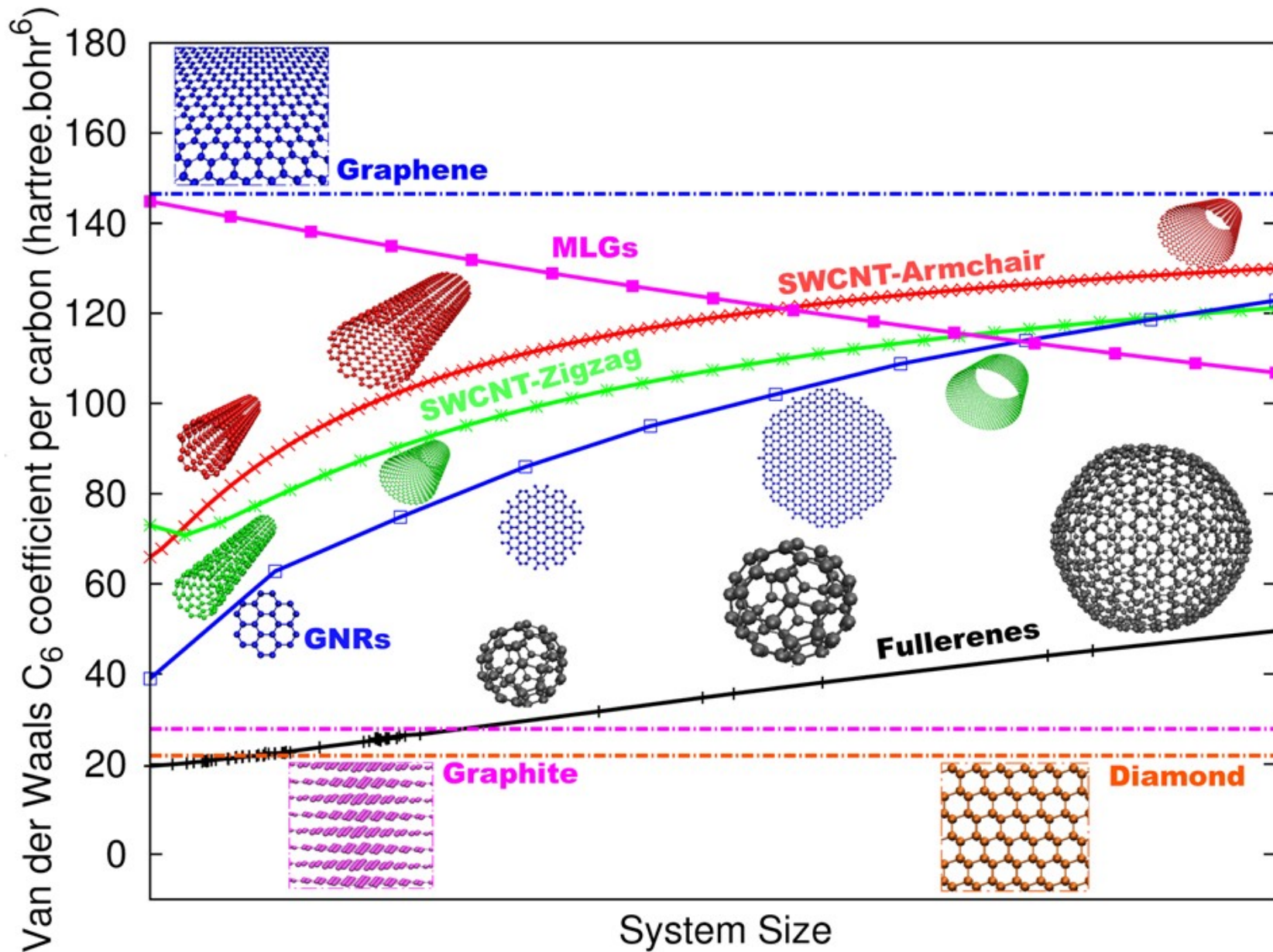
Electrodynamemic treatment of vdW interactions: beyond “hybridized atoms”



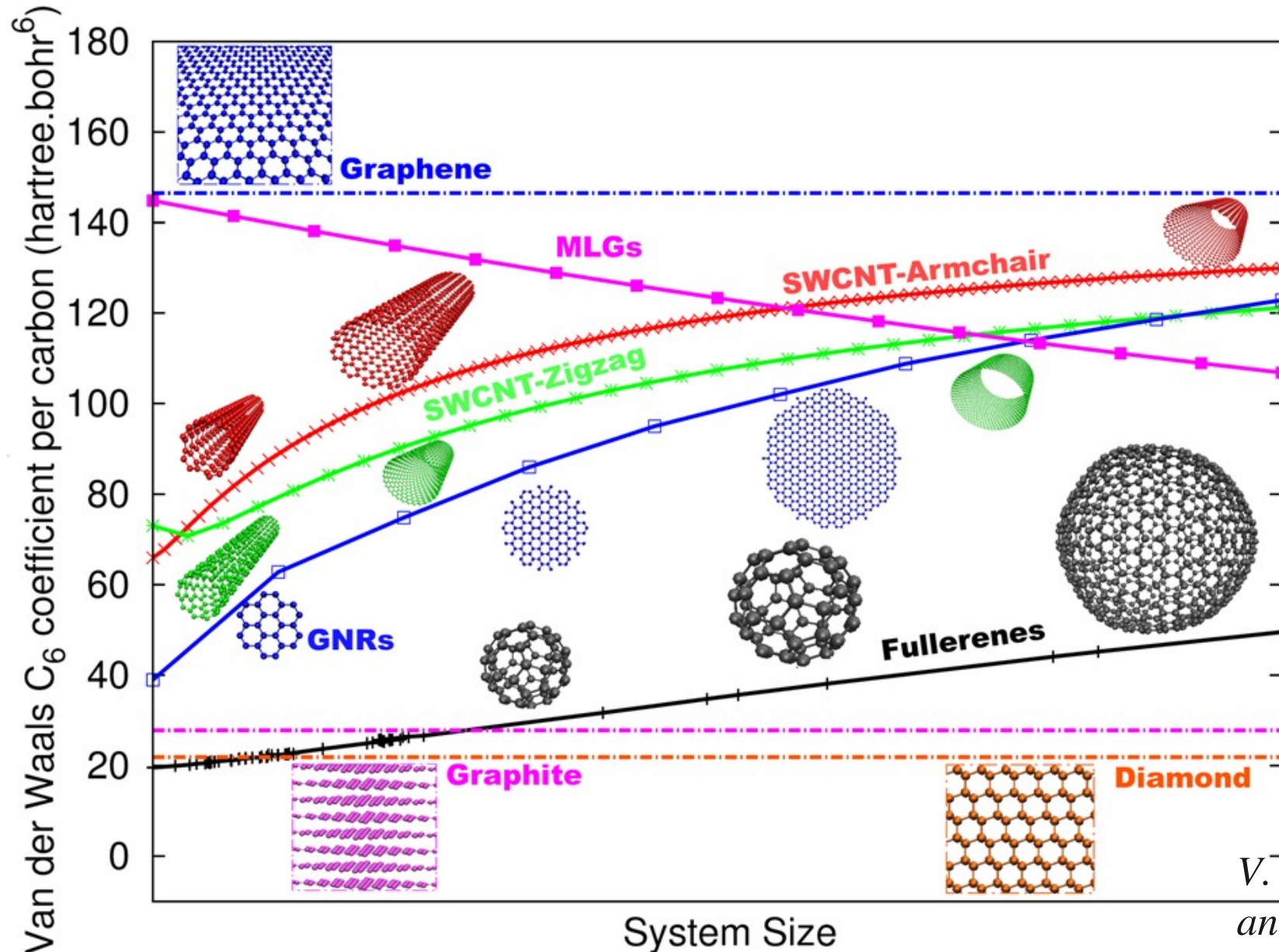
Electrodynamic treatment of vdW interactions: beyond “hybridized atoms”



Electrodynamic treatment of vdW interactions: beyond “hybridized atoms”



Electrodynamic treatment of vdW interactions: beyond “hybridized atoms”

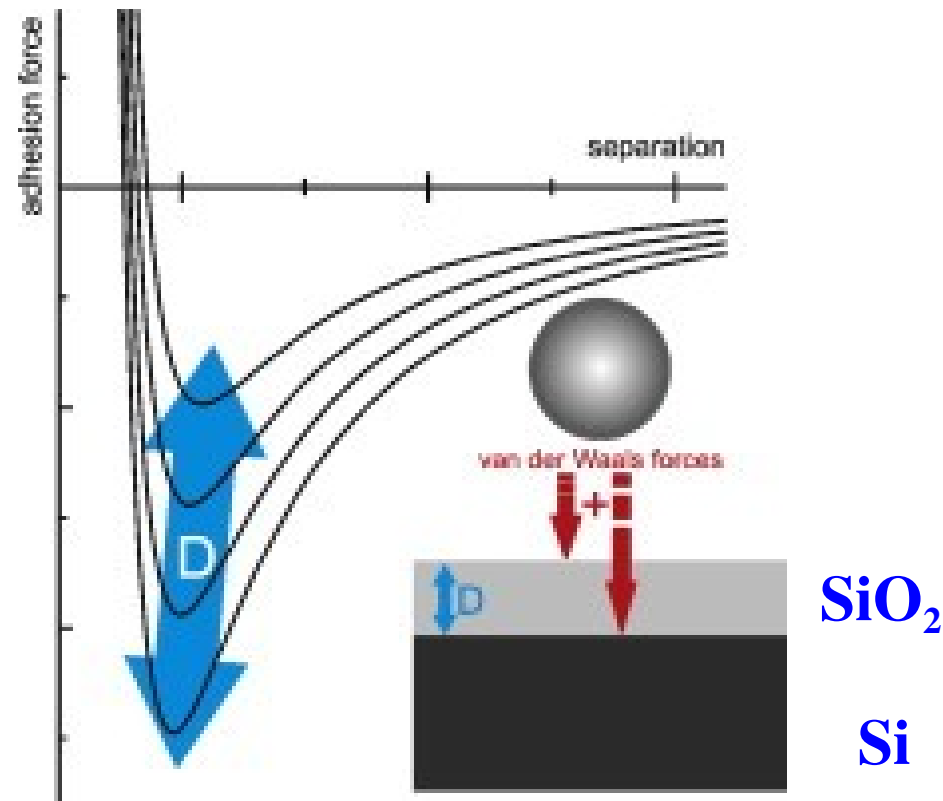


Vivek
Gobre

V. V. Gobre
and A. Tkatchenko,
Nature Comm. (2013)

How long-ranged are vdW interactions? ...

Direct experimental evidence

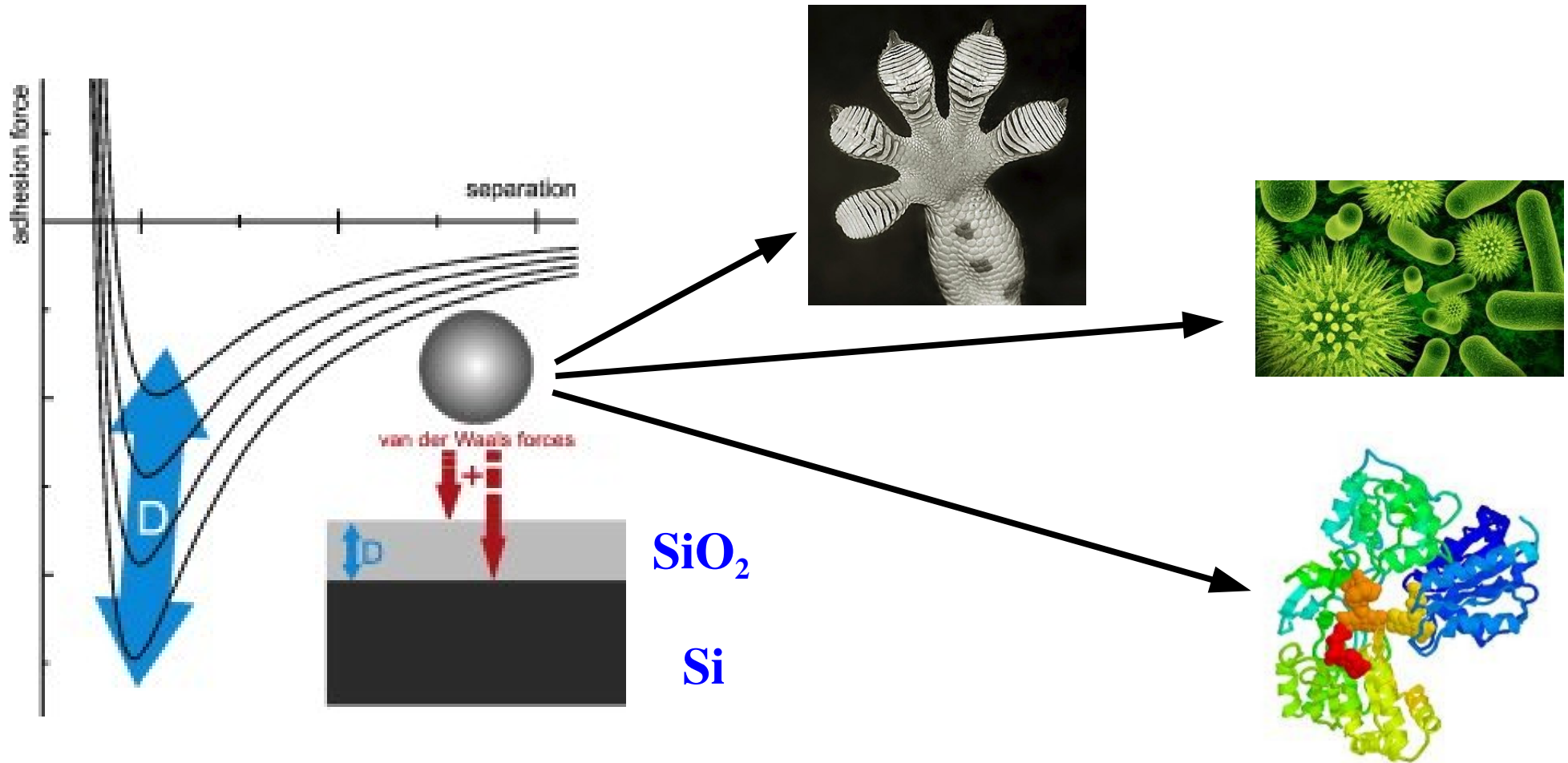


P. Loskill, H. Hähl, T. Faidt, S. Grandthyll, F. Müller, and K. Jacobs, Adv. Coll. Interf. Sci. 107, 179182 (2012).

P. Loskill, J. Puthoff, M. Wilkinson, K. Mecke, K. Jacobs and K. Autumn, J. R. Soc. Interface, to be published (2013).

How long-ranged are vdW interactions? ...

Direct experimental evidence



P. Loskill, H. Hähl, T. Faidt, S. Grandthyll, F. Müller, and K. Jacobs, Adv. Coll. Interf. Sci. 107, 179182 (2012).

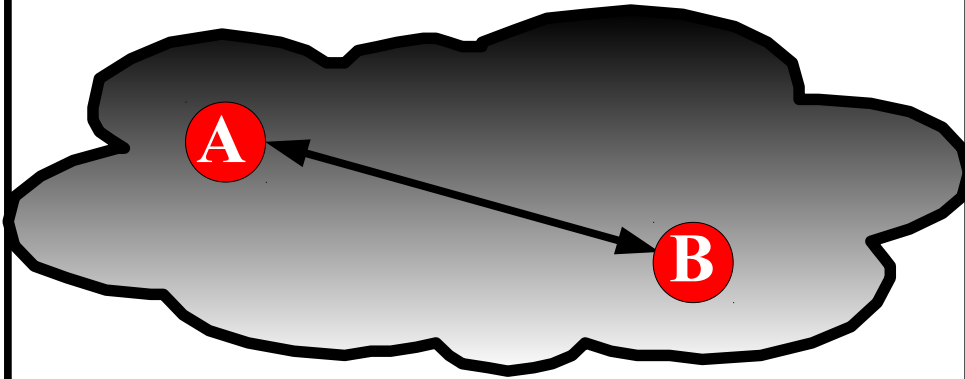
P. Loskill, J. Puthoff, M. Wilkinson, K. Mecke, K. Jacobs and K. Autumn, J. R. Soc. Interface, to be published (2013).

Towards Efficient Many-Body Treatment of vdW Interactions

The conventional approach

(*Grimme, Johnson-Becke/Corminboeuf,
Tkatchenko-Scheffler, Langreth-Lundqvist
vdW-DF, Vydrov-van Voorhis, ...*)

Effective screening and
two-body energy



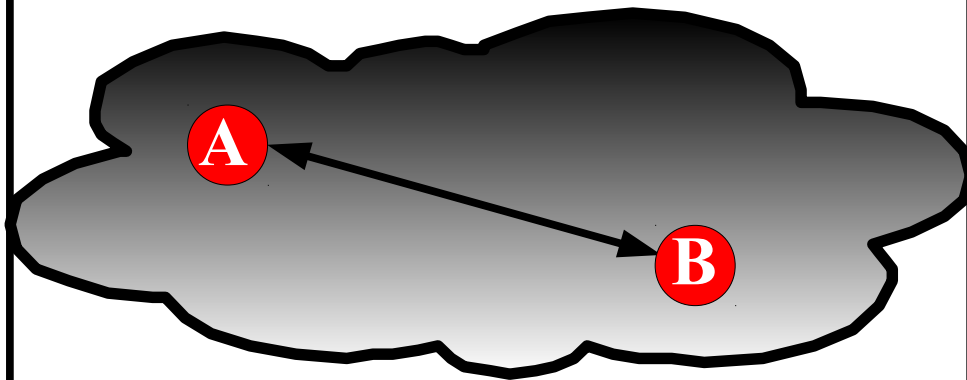
Valid for small molecules *or*
homogeneous dielectrics

Towards Efficient Many-Body Treatment of vdW Interactions

The conventional approach

(*Grimme, Johnson-Becke/Corminboeuf, Tkatchenko-Scheffler, Langreth-Lundqvist vdW-DF, Vydrov-van Voorhis, ...*)

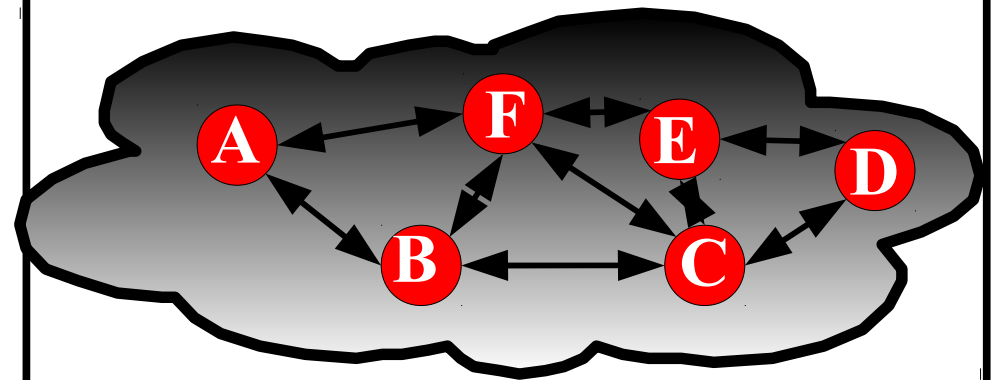
Effective screening and two-body energy



Valid for small molecules *or* homogeneous dielectrics

The new state-of-the-art:

Full many-body response and energy for a system of quantum oscillators (**DFT+MBD**)



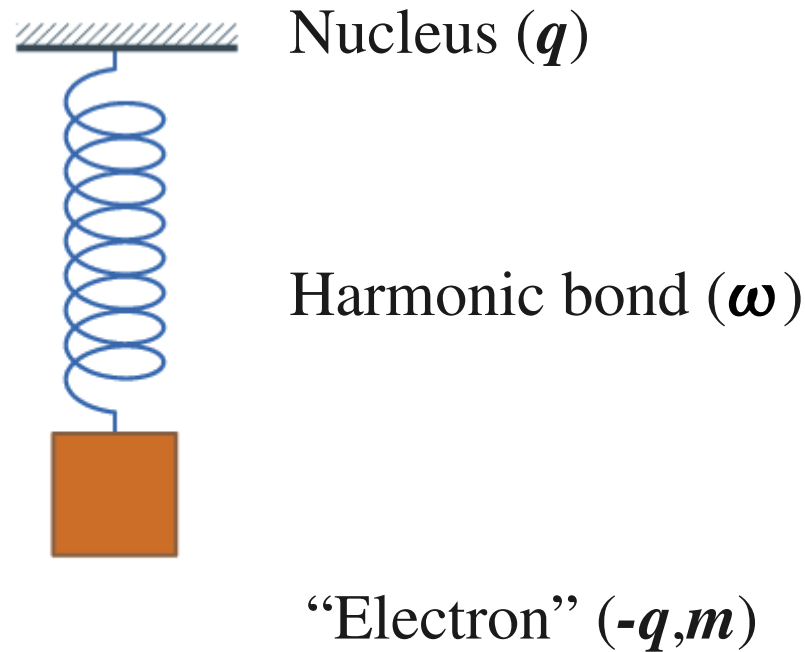
Valid for **small and large molecules, insulators, metals, interfaces, ...**

A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* (2009).

A. Tkatchenko, R. A. DiStasio Jr., R. Car, M. Scheffler, *Phys. Rev. Lett.* (2012).

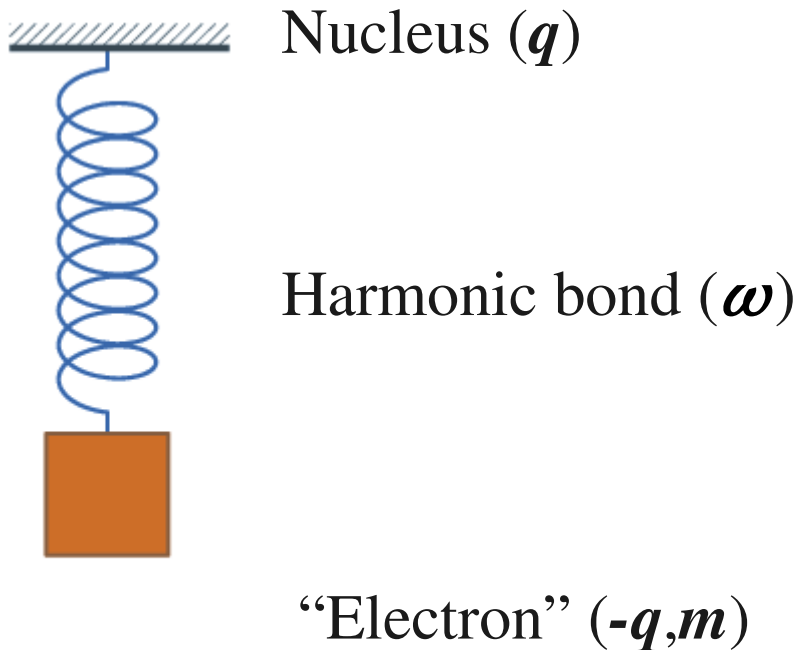
R. A. DiStasio Jr., O. A. von Lilienfeld, A. Tkatchenko, *Proc. Natl. Acad. Sci.* (2012).

The Model: Quantum Harmonic Oscillator (QHO)



Model proposed by *W. L. Bade* (1957); and used by *B. J. Berne*; *A. Donchev*; *M. W. Cole*; *G. Martyna*; *K. Jordan*; and others.

The Model: Quantum Harmonic Oscillator (QHO)

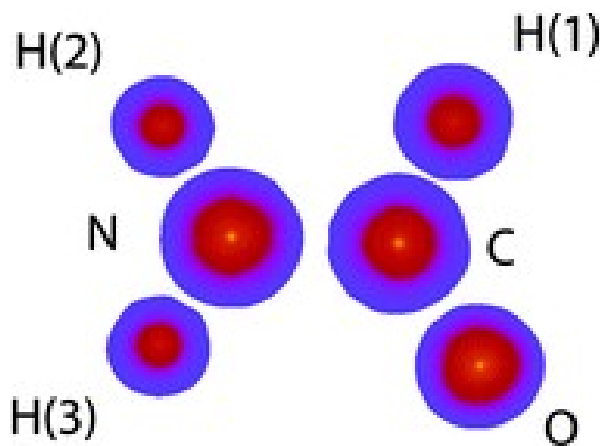


In the dipole approximation:
 (α, ω) fully characterize the QHO

Model proposed by *W. L. Bade* (1957); and used by *B. J. Berne*; *A. Donchev*; *M. W. Cole*; *G. Martyna*; *K. Jordan*; and others.

First-Principles Model: QHOs in Molecules and Solids

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



$$\alpha_A(i\omega) = \frac{\alpha_A^0}{1 + (\omega/\omega_A^0)^2}$$

α^0 and ω^0 include short-range hybridization

$$C_6 = C_6[n(\mathbf{r})], \quad R_{\text{vdW}} = R_{\text{vdW}}[n(\mathbf{r})]$$

A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. (2009)

The Method: DFT+MBD

TS-vdW method

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

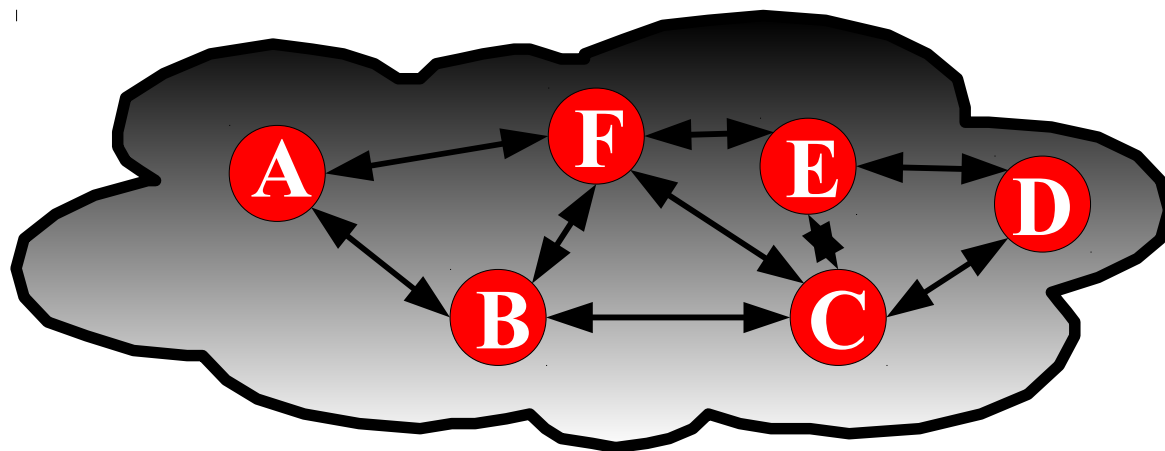
Self-consistent electrodynamic response (Dyson)

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

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

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

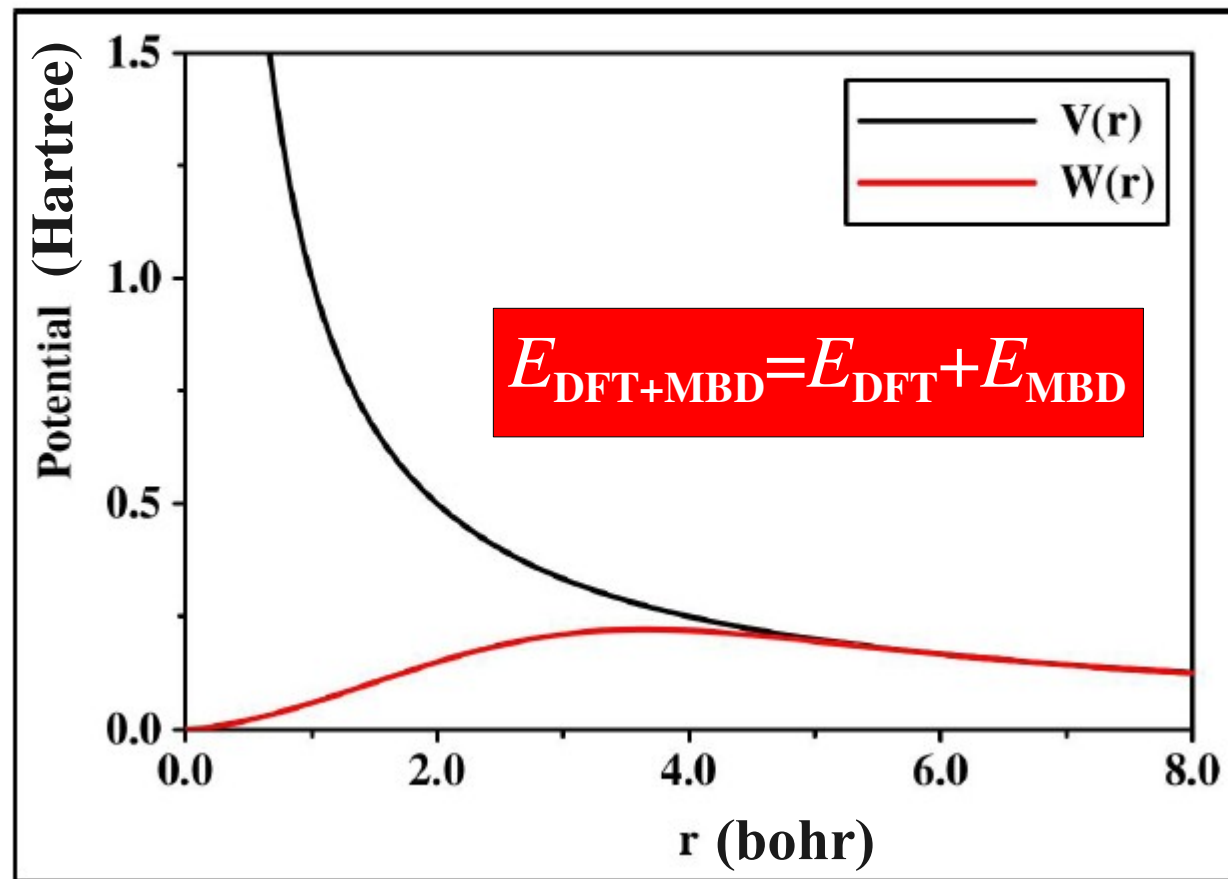
Salient Features of the MBD Method



- Seamless treatment of short-range (quantum) and long-range (classical) electrodynamic response
- Full correlation energy of coupled QHOs is equivalent to the random-phase approximation or ring-CCD (*JCP* 138, 074106 (2013))
- Computes many-body vdW energy to *infinite order*
- Negligible computational cost compared to DFT (MBD calculations can be easily done for > 10,000 atoms)

Coupling DFT and MBD by range separation of the Coulomb potential

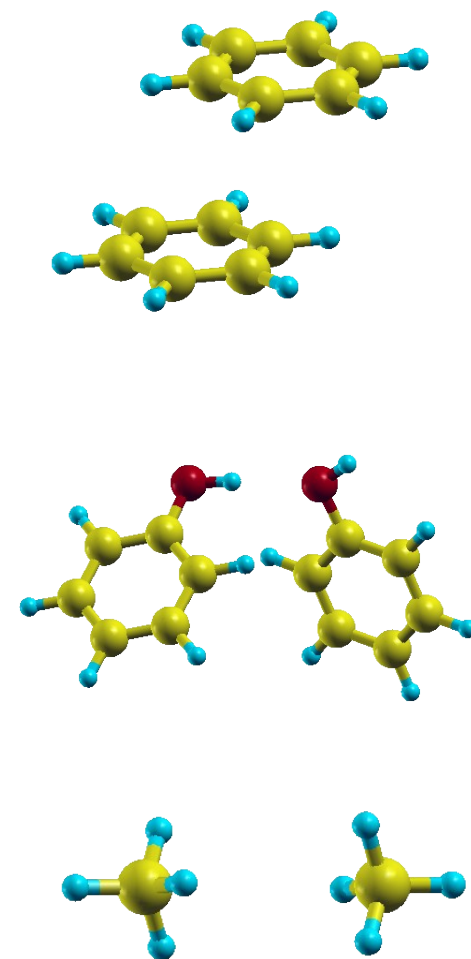
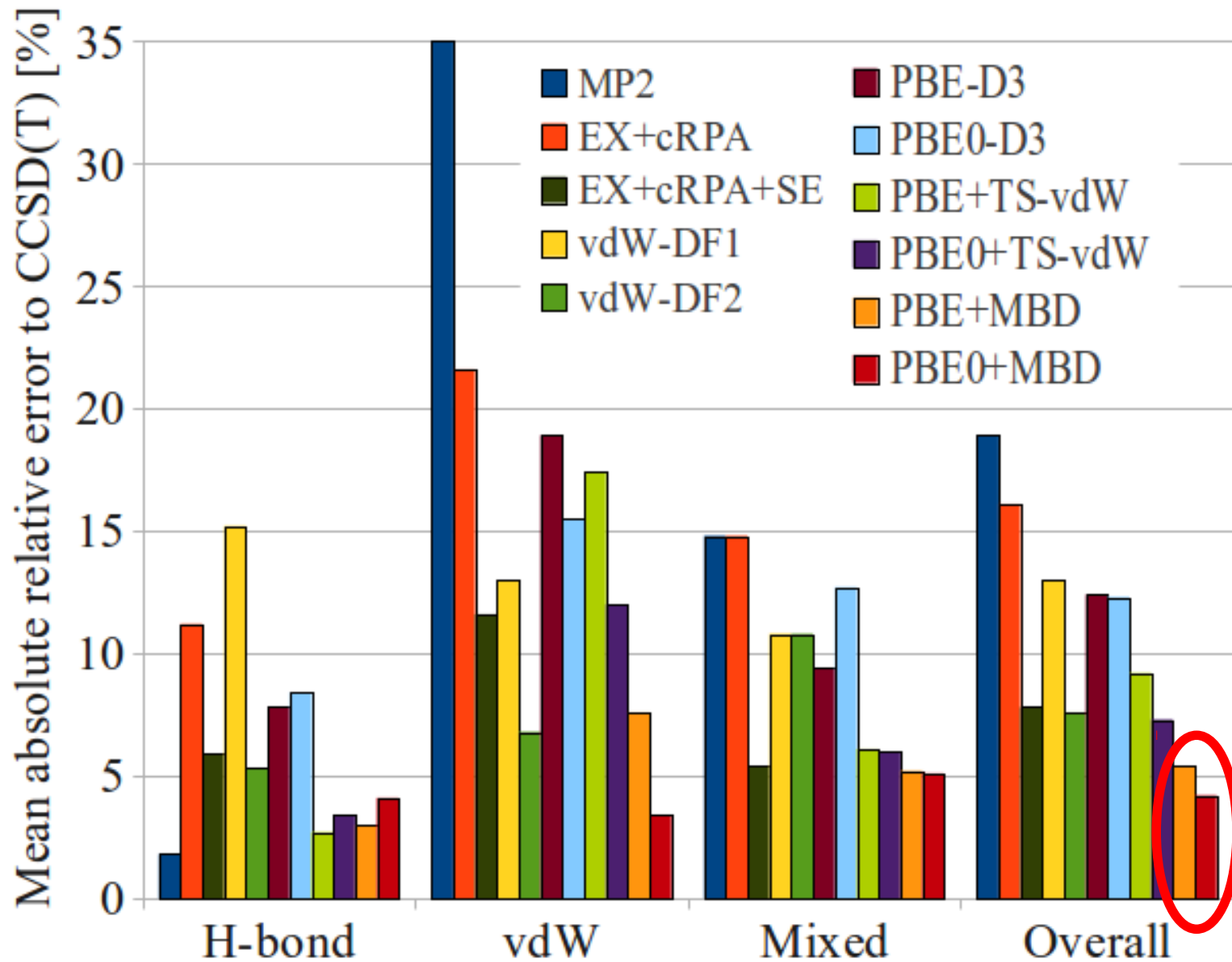
$$W(r_{pq}) = \left(1 - \exp\left(-\left(r_{pq}/R_{pq}^{\text{vdW}}\right)^\beta\right)\right) / r_{pq}$$



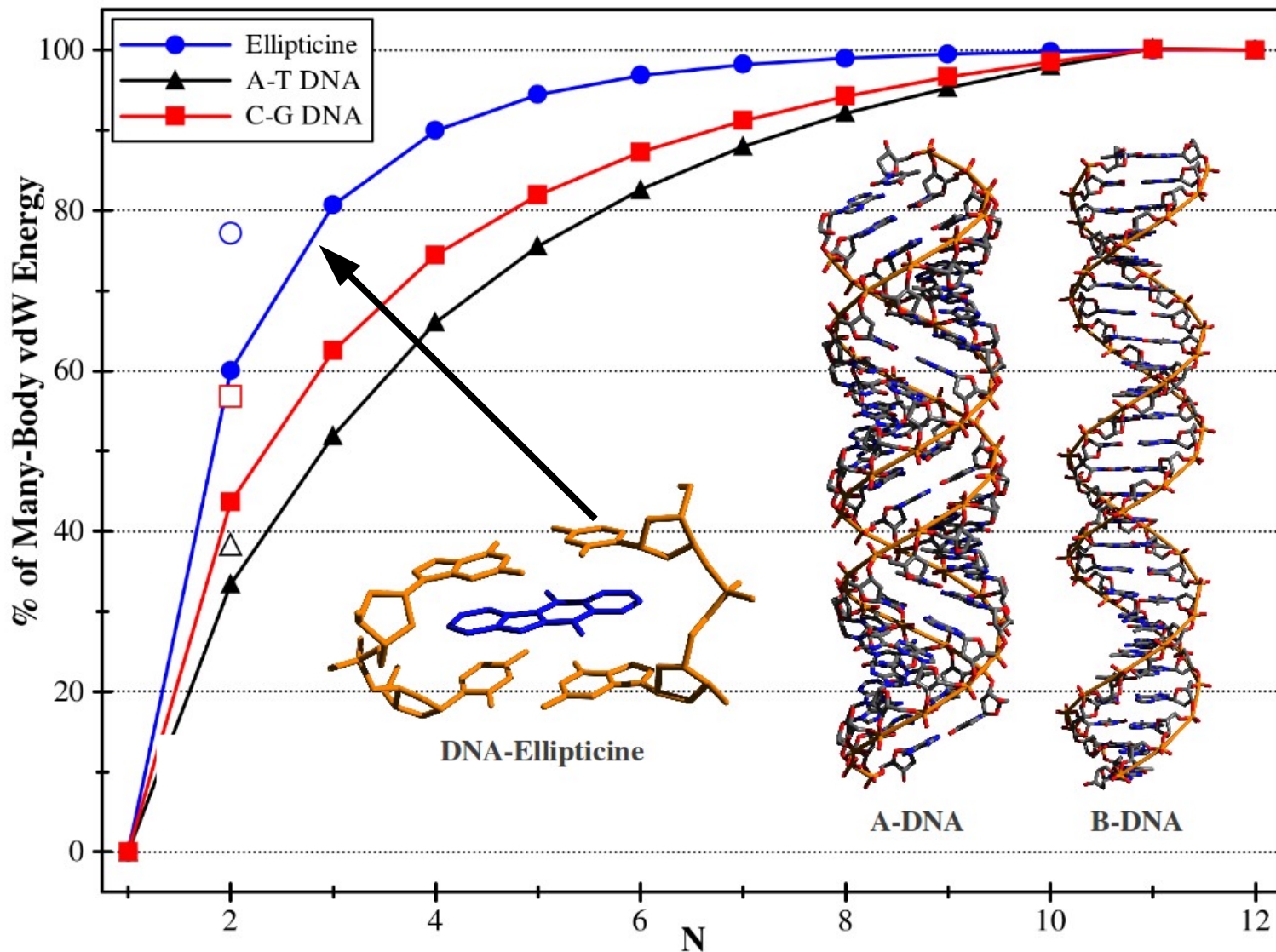
See work on range separation by A. Savin, H. Stoll, G. Scuseria, K. Hirao, ...

Performance of DFT+MBD

for gas-phase intermolecular interactions



Large many-body vdW effects in complex molecular geometries



O. A. von Lilienfeld
(U. Basel)



Robert DiStasio Jr.
(Princeton)

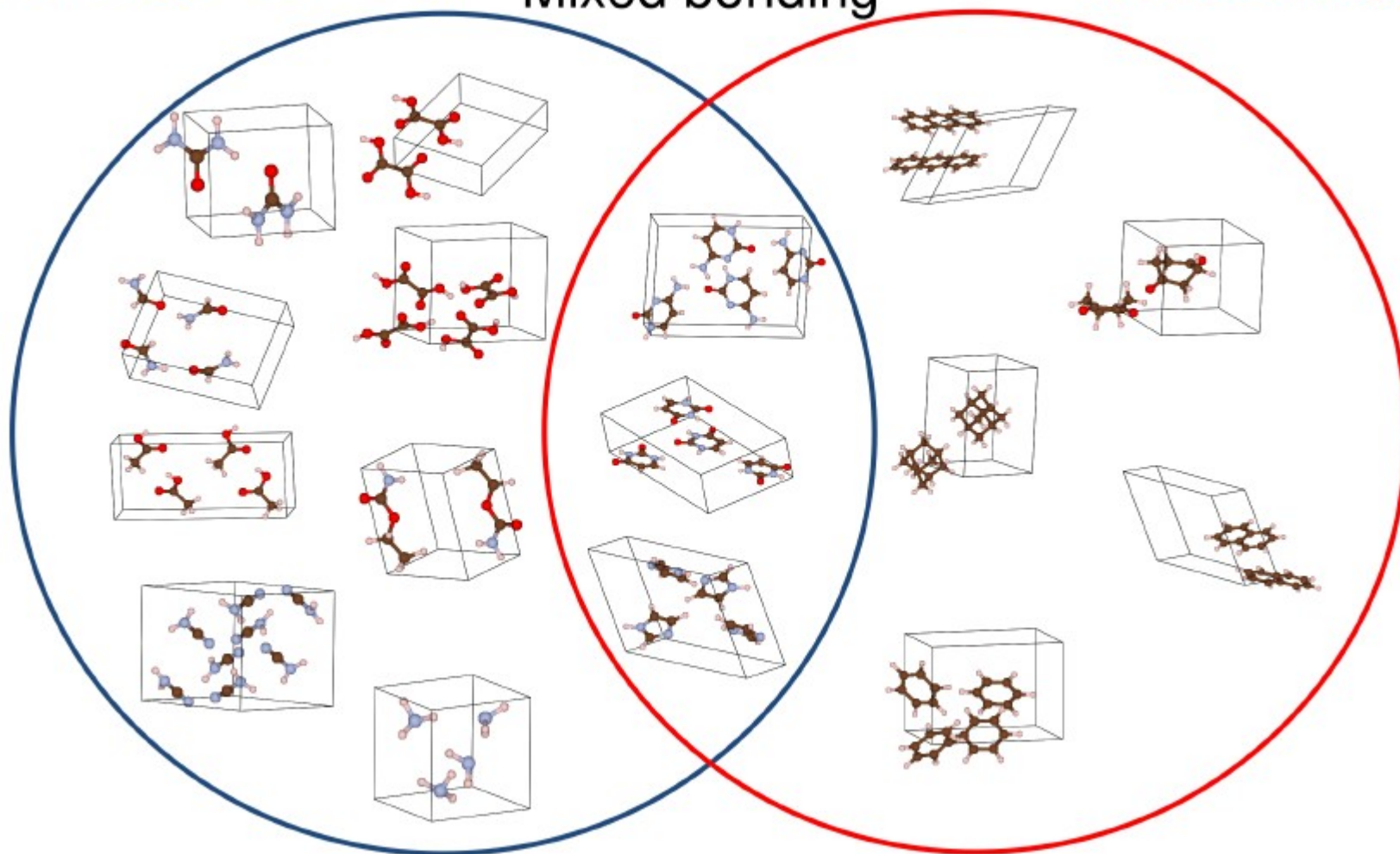
R. A. DiStasio Jr., O. A. von Lilienfeld, and A. Tkatchenko, PNAS (2012)

“Chemically Accurate” Predictions for Molecular Materials

Hydrogen bonding

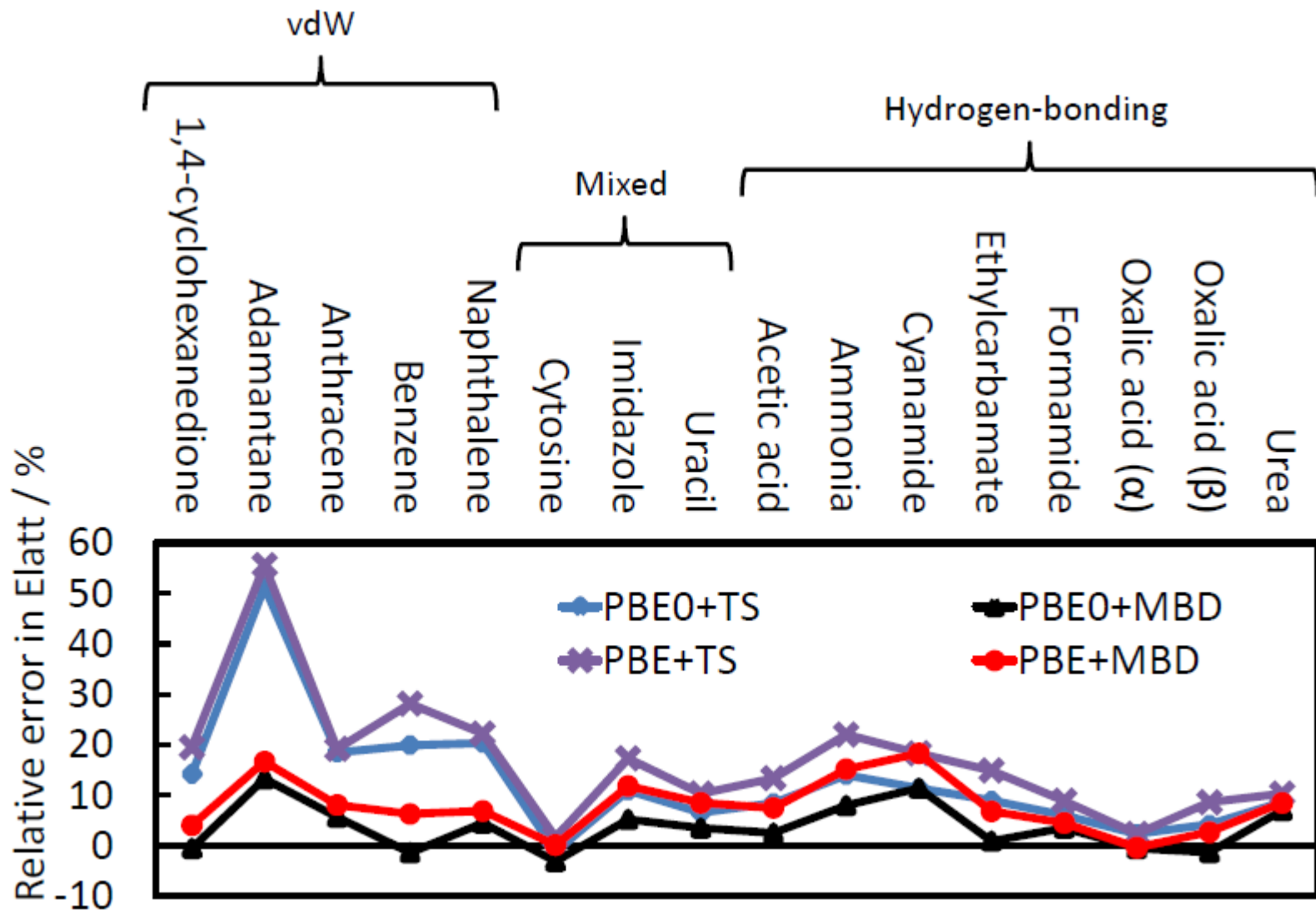
Mixed bonding

vdW bonding



*A. M. Reilly and A. Tkatchenko, **J. Phys. Chem. Lett.** 4, 1028 (2013);
J. Chem. Phys. 139, 024705 (2013).*

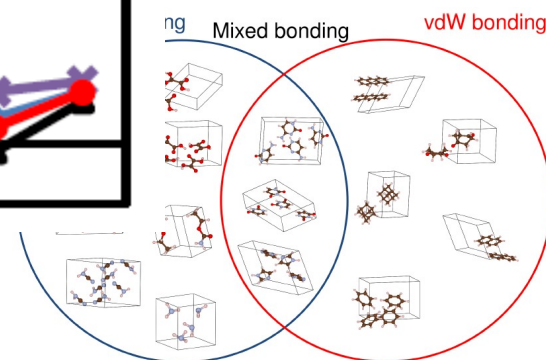
“Chemically Accurate” Predictions for Molecular Materials



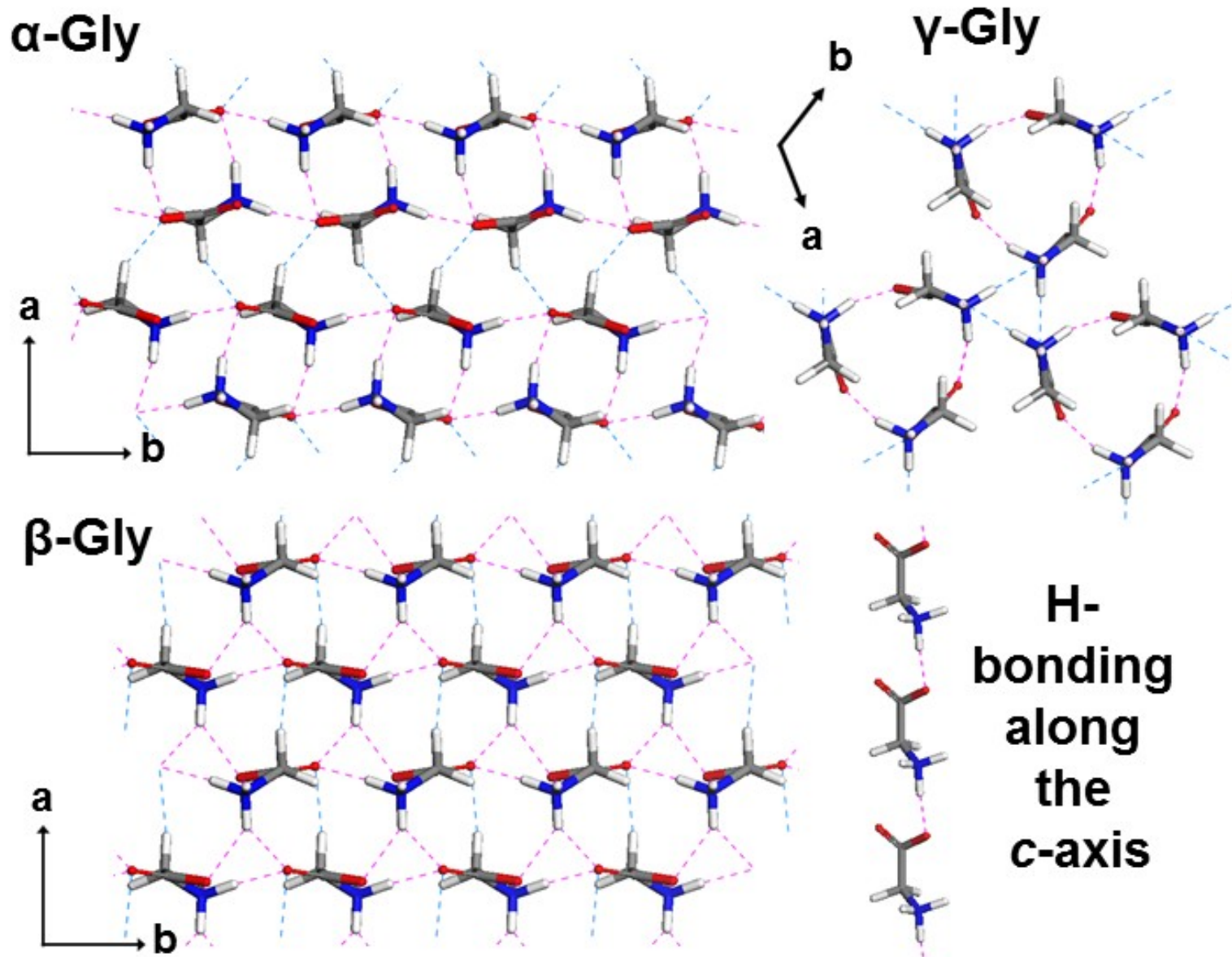
**Anthony
Reilly**

PBE0+MBD overall accuracy: 0.8 kcal/mol; 4.6%

A. M. Reilly and A. Tkatchenko, *J. Phys. Chem. Lett.* **4**, 1028 (2013).

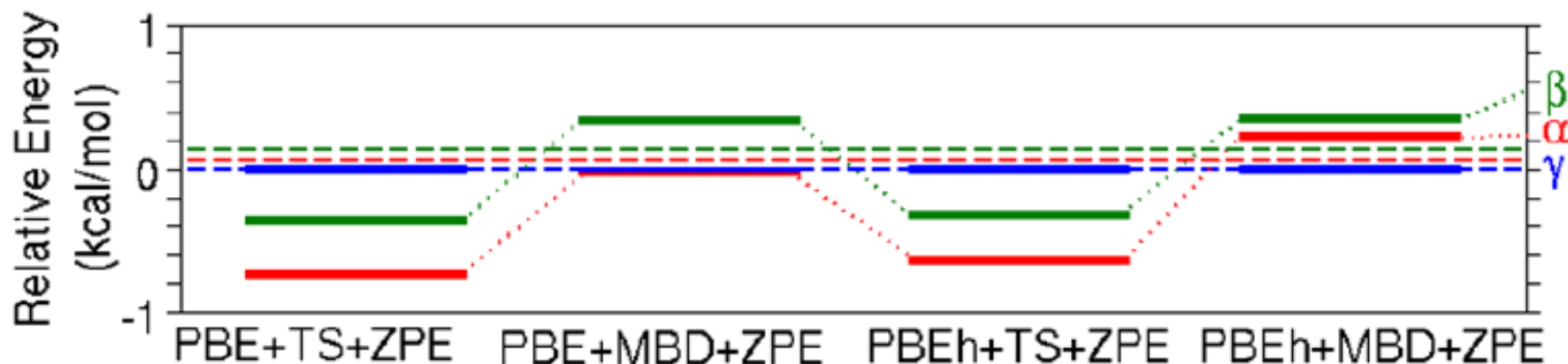
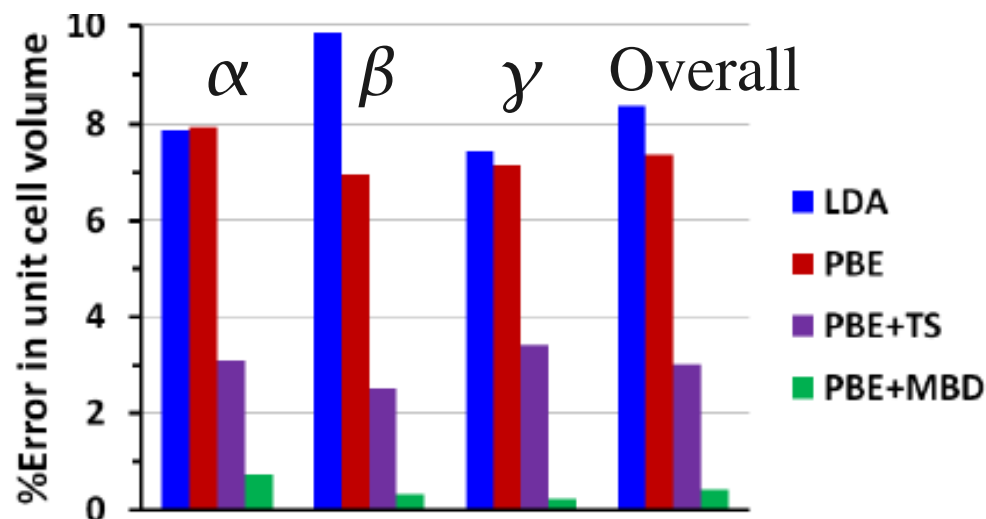


DFT+MBD correctly discriminates between crystal polymorphs: Example of glycine



DFT+MBD correctly discriminates between crystal polymorphs: Example of glycine

MBD reduces the error in the unit cell volume to less than 0.8%!

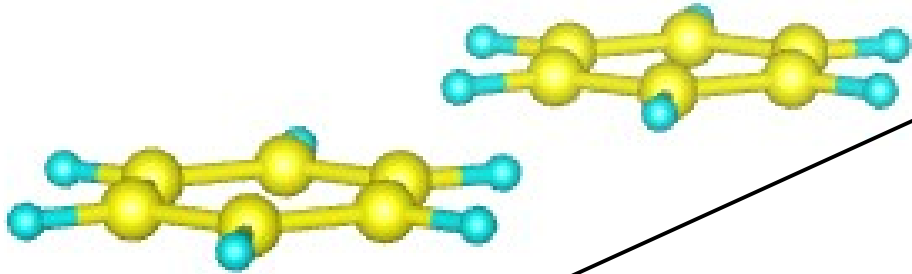


DFT+MBD gives relative energies in excellent agreement with experiment, reaching an accuracy better than 0.3 kcal/mol!

N. Marom, R. A. DiStasio, Jr., V. Atalla, S. Levchenko, A.M. Reilly, J. R. Chelikowsky, L. Leiserowitz, and A. Tkatchenko, *arXiv: 1210.5636*
Angew. Chem. (2013).

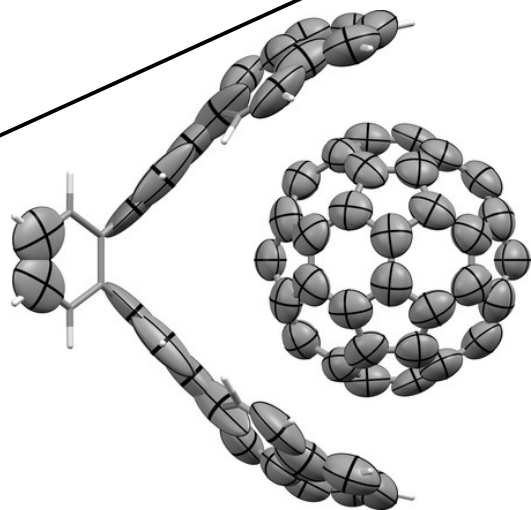
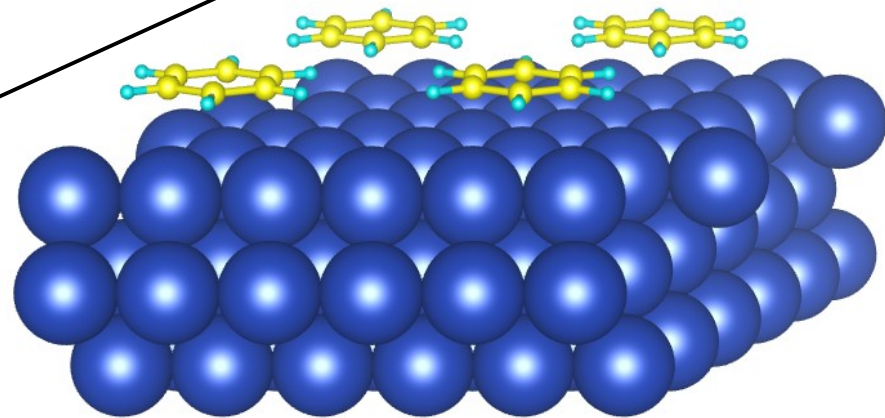
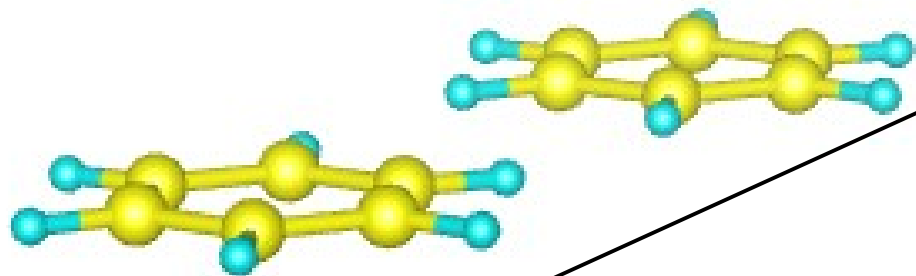
Summary

$$C_{6,\text{eff}}^{ii} = C_{6,\text{eff}}^{ii}[n(\mathbf{r})]$$



Summary

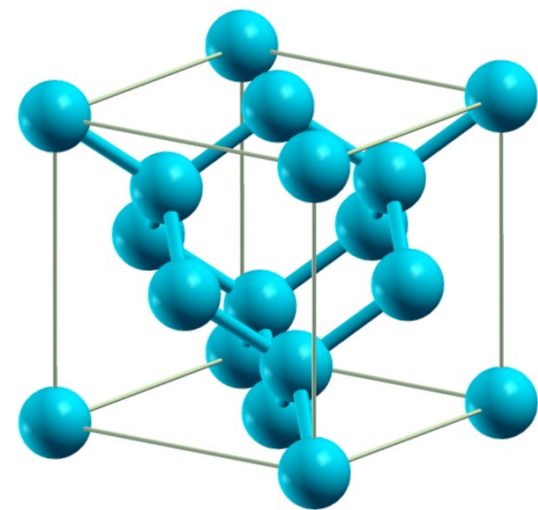
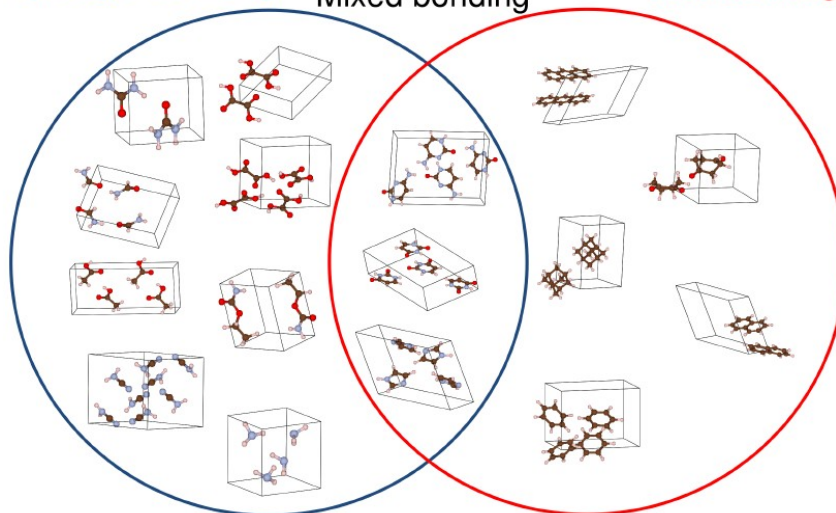
$$C_{6,\text{eff}}^{ii} = C_{6,\text{eff}}^{ii}[n(\mathbf{r})]$$



Hydrogen bonding

Mixed bonding

vdW bonding



$$E_c = - \int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \text{Tr} \left((\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; i\omega) - \chi_0(\mathbf{r}_1, \mathbf{r}_2; i\omega)) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

Summary

$$C_{6,\text{eff}}^{ii} = C_{6,\text{eff}}^{ii}[n(\mathbf{r})]$$

First step towards general treatment of vdW interactions in molecules and condensed matter.

Many possible extensions:

Delocalized excitations

Relativistic effects (retardation)

Finite temperature

Higher multipole effects

Systematic scaling to larger systems

...

$$E_c = - \int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \text{Tr} \left((\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; i\omega) - \chi_0(\mathbf{r}_1, \mathbf{r}_2; i\omega)) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

Summary

$$C_{6,\text{eff}}^{ii} = C_{6,\text{eff}}^{ii}[n(\mathbf{r})]$$

First step towards general treatment of vdW interactions in molecules and condensed matter.

Many possible extensions:

Delocalized excitations

Relativistic effects (retardation)

Finite temperature

Higher multipole effects

Systematic scaling to larger systems

...

FHI-aims: “many_body_dispersion”

$$E_c = - \int_0^\infty \frac{1}{2\pi} \int_0^{2\pi} \int_0^{2\pi} \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$