When (2 + 2) ≠ 4 ?

Alexandre Tkatchenko

Fritz-Haber-Institut der Max-Planck-Gesellschaft,

Berlin, Germany

QMC@TTI, **Apuan Alps, Jul 29, 2013**

When (2 + 2) ≠ 4

or

Van der Waals Interactions in Complex (and Simple) Materials

Alexandre Tkatchenko

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Acknowledgments

Robert A. DiStasio

Matthias Scheffler

Anatole von Lilienfeld

Roberto Car

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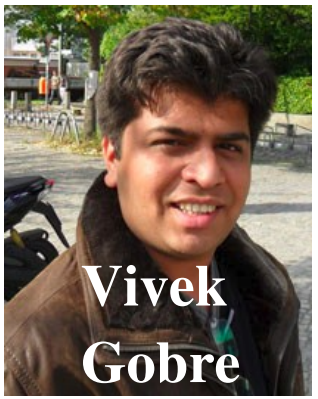
Alberto Ambrosetti



Anthony Reilly

Textbook picture of vdW interactions

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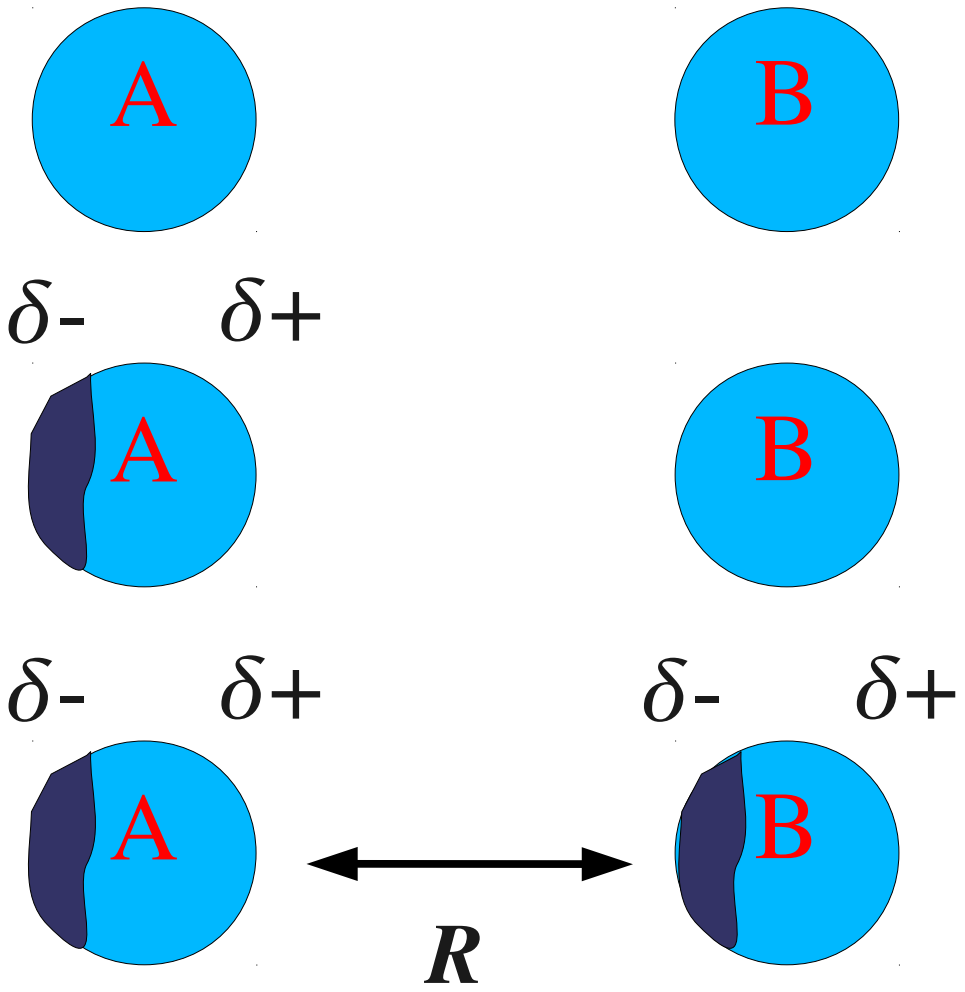
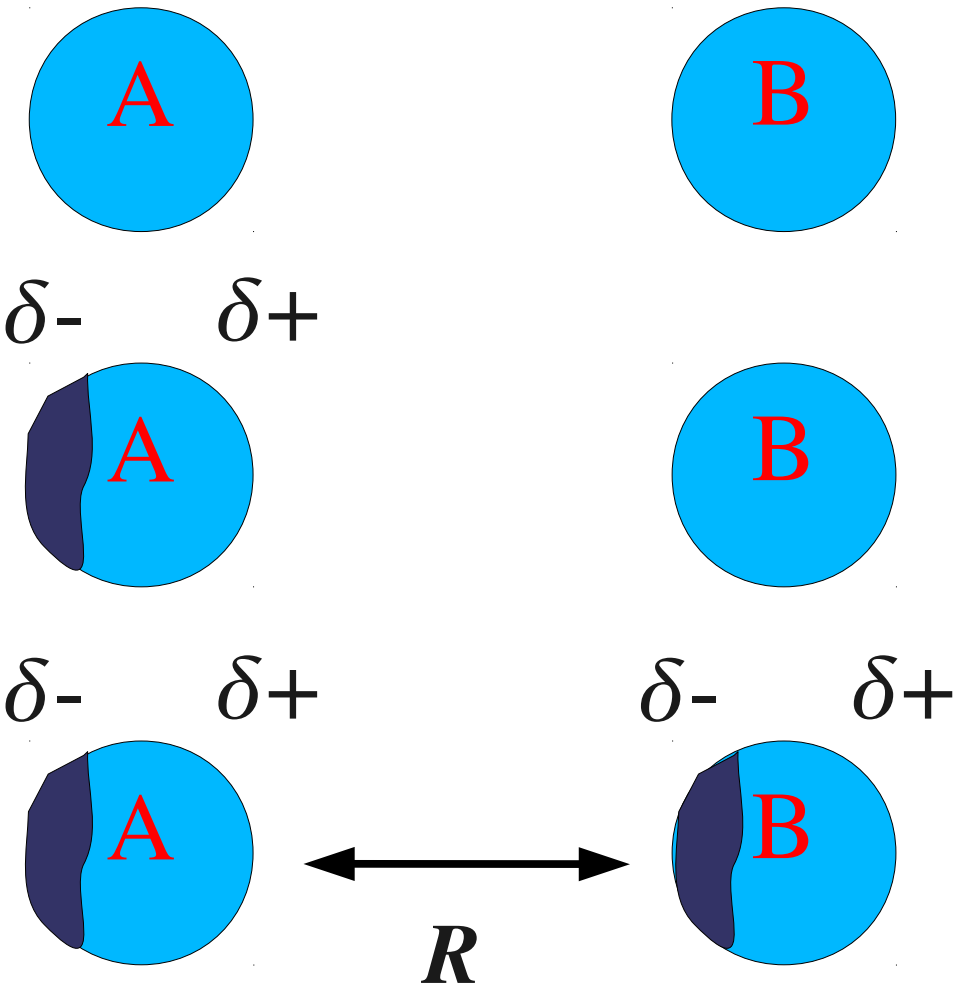


Textbook picture of vdW interactions



$$E^{(2)}_{\mathrm{vdW}} = -\frac{C_6^{\mathrm{AB}}}{R^6_{\mathrm{AB}}} \rightarrow C_6^{\mathrm{AB}} = \frac{3}{\pi}\int \alpha_{\mathrm{A}}(i\omega)\alpha_{\mathrm{B}}(i\omega)d\omega$$

Reality check for vdW from experiment

PRL **110,** 263201 (2013)

Selected for a Viewpoint in *Physics*
PHYSICAL REVIEW LETTERS

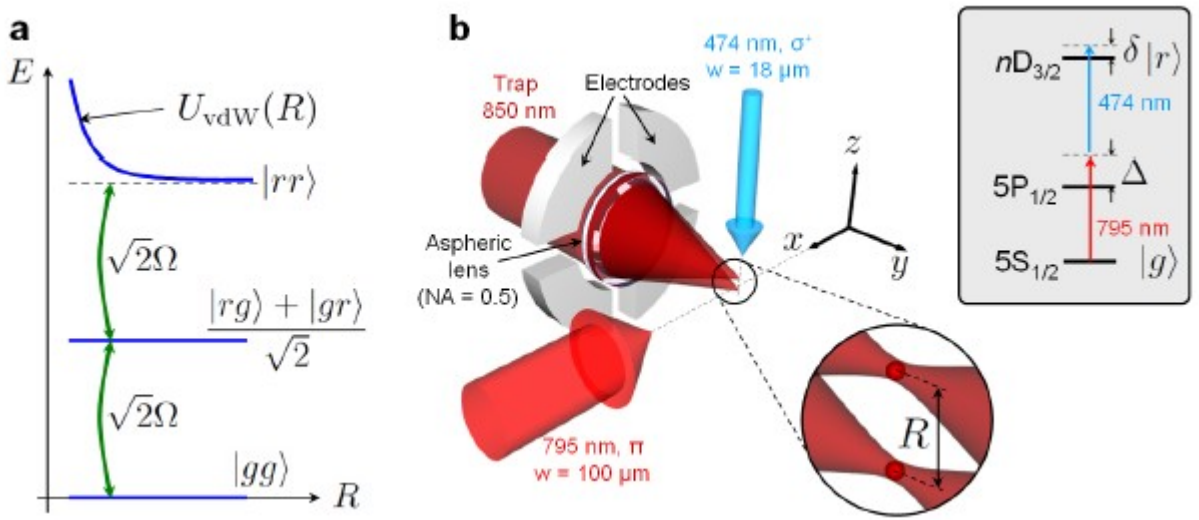
week ending
28 JUNE 2013

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

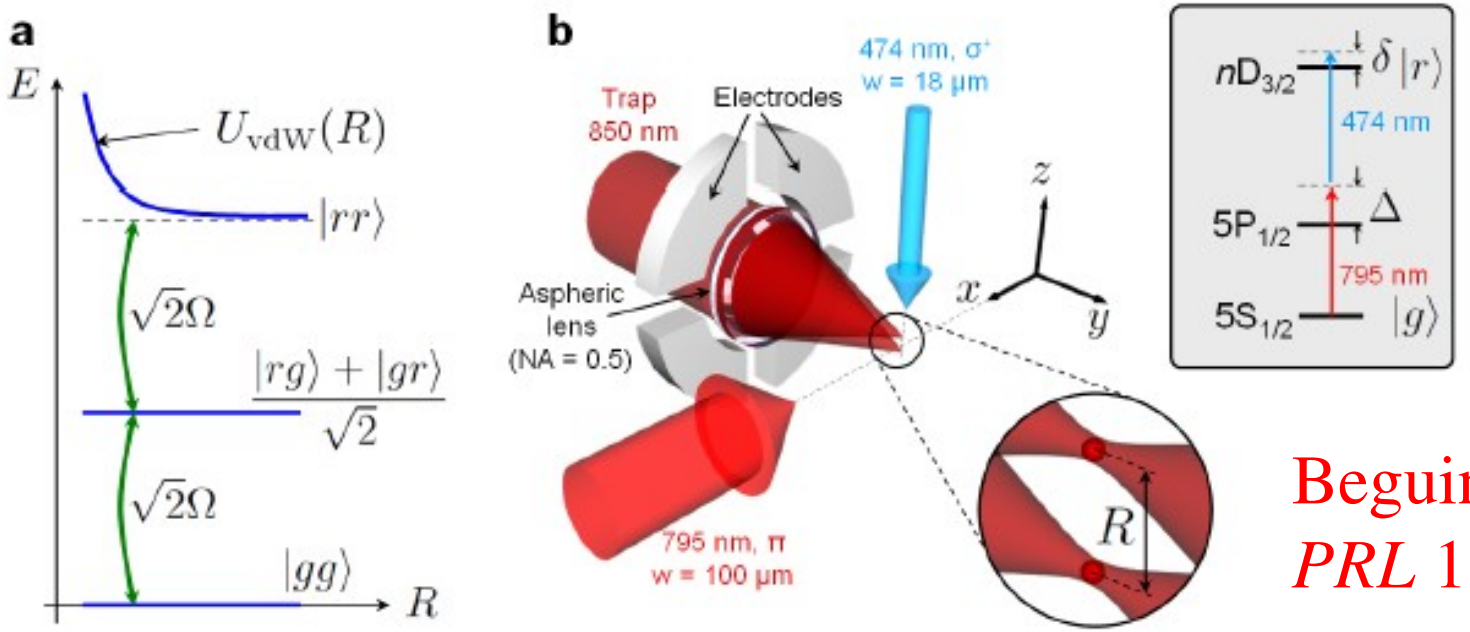
L. Béguin,[1] A. Vernier,[1] R. Chicireanu,[2] T. Lahaye,[1] and A. Browaeys[1]

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



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



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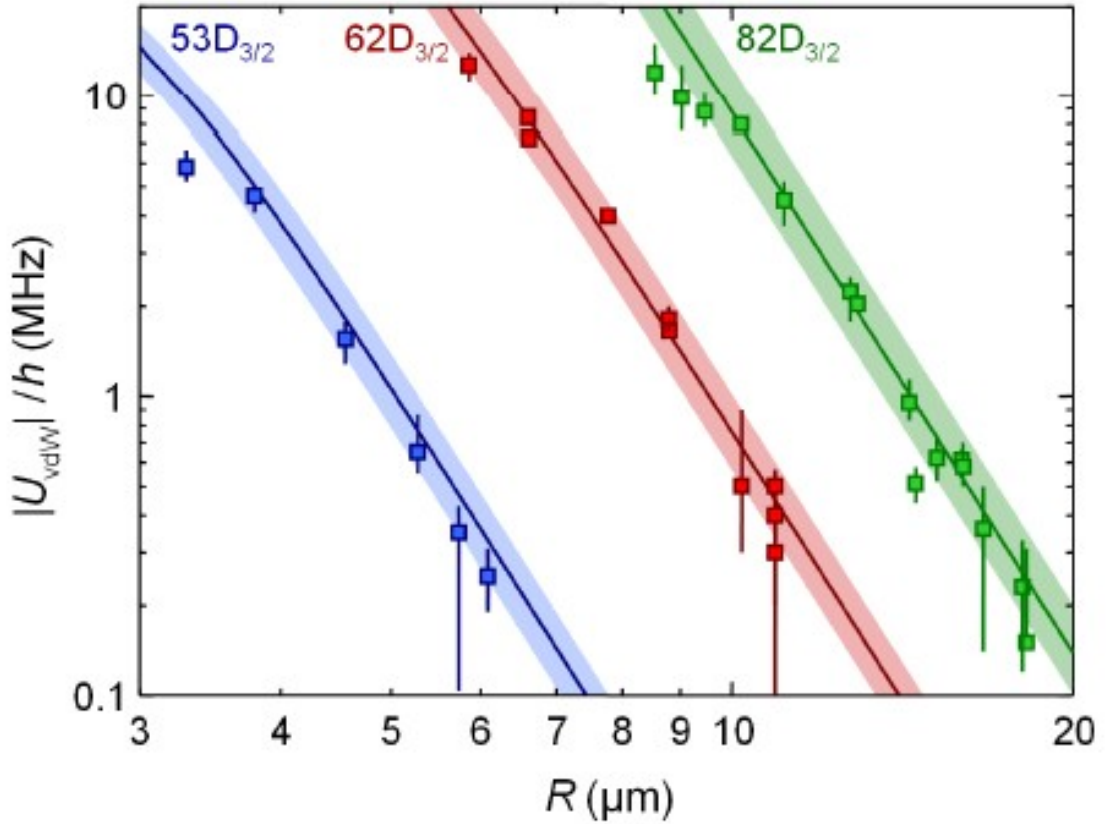
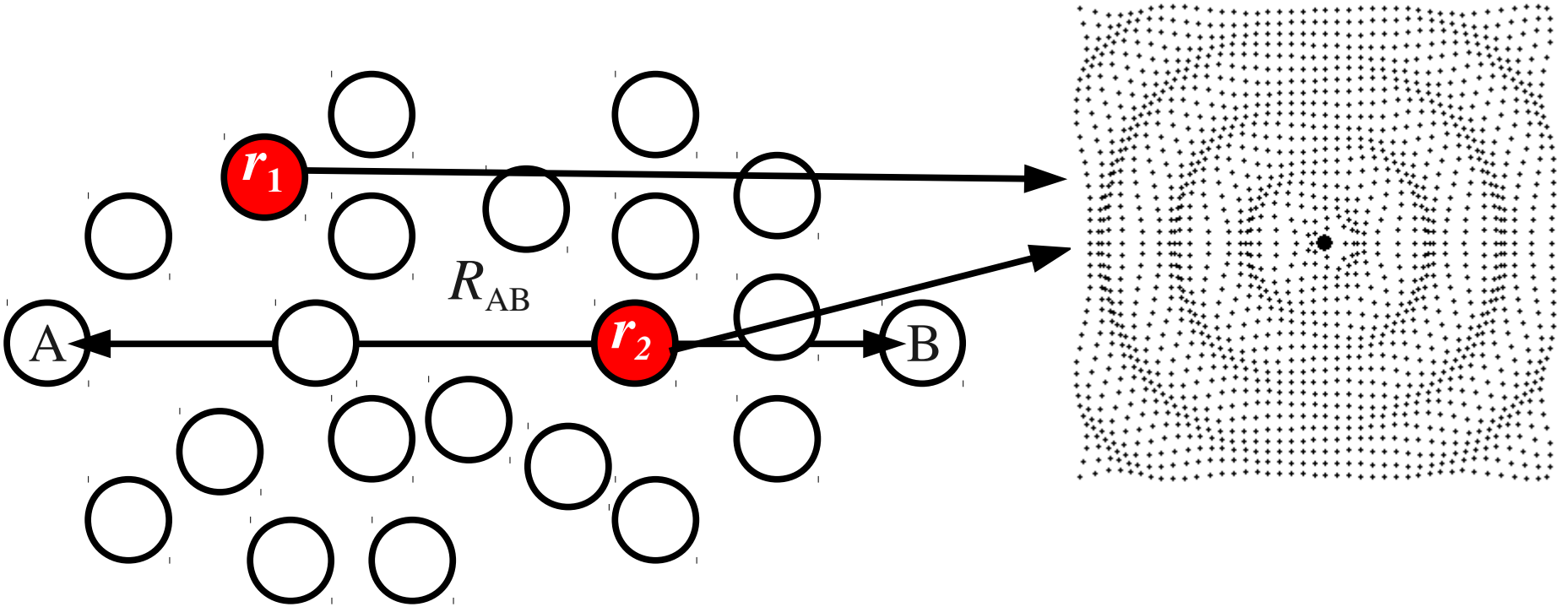
PRL 110, 263201 (2013).



Beyond textbook model of vdW interactions: Electrodynamic response effects



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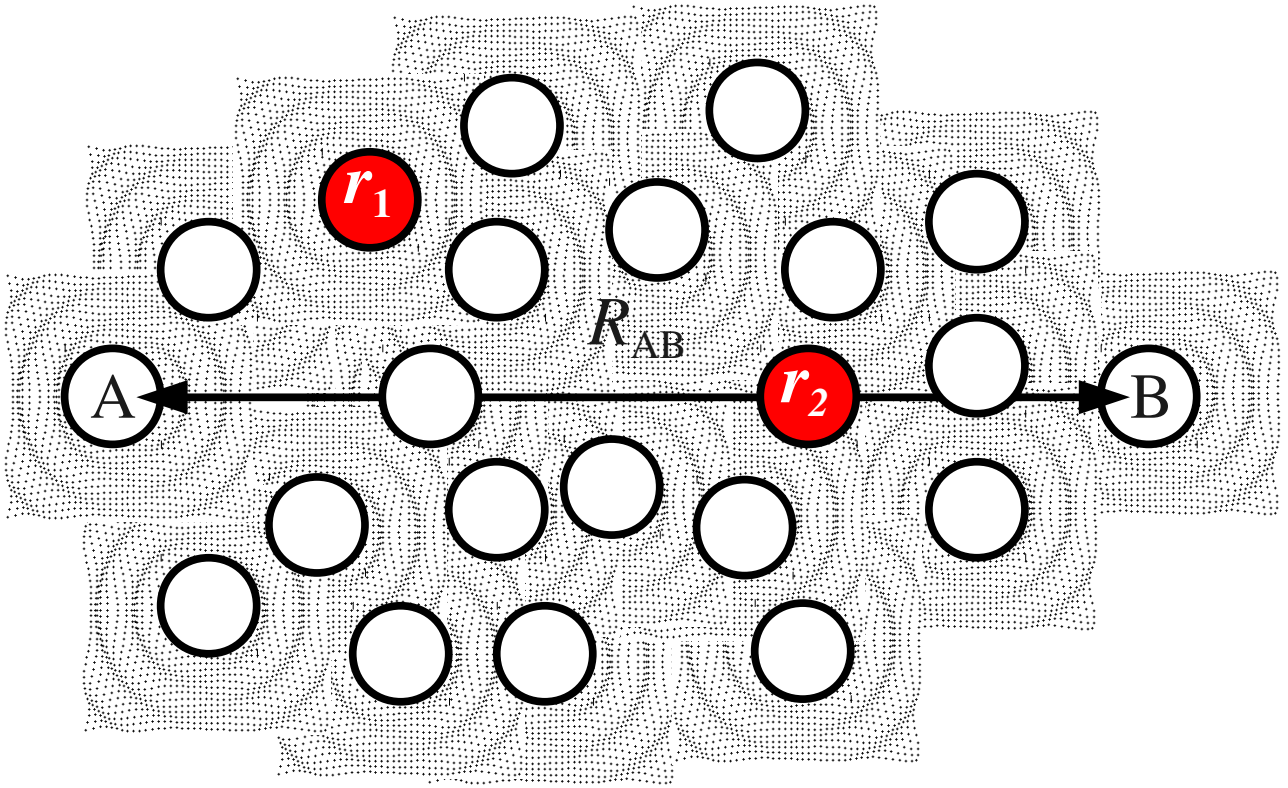
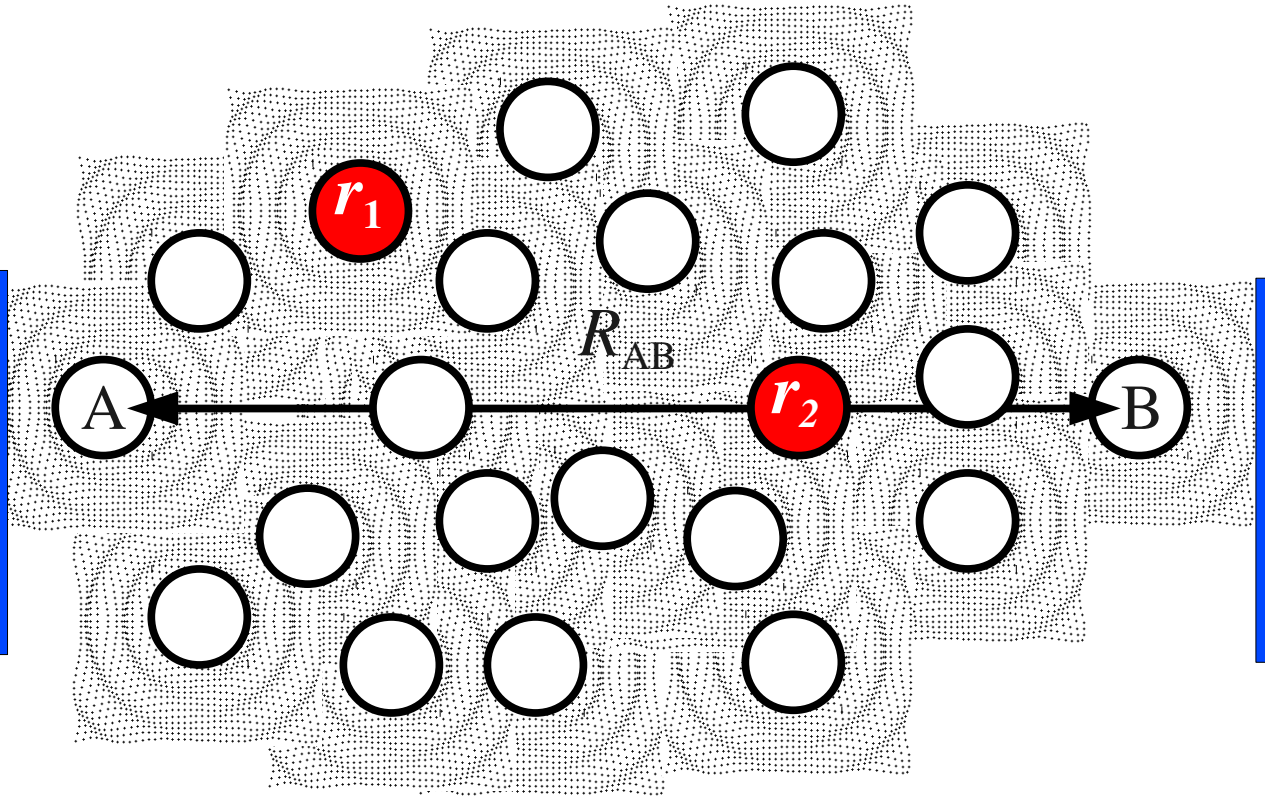


Beyond textbook model of vdW interactions: Electrodynamic response effects

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

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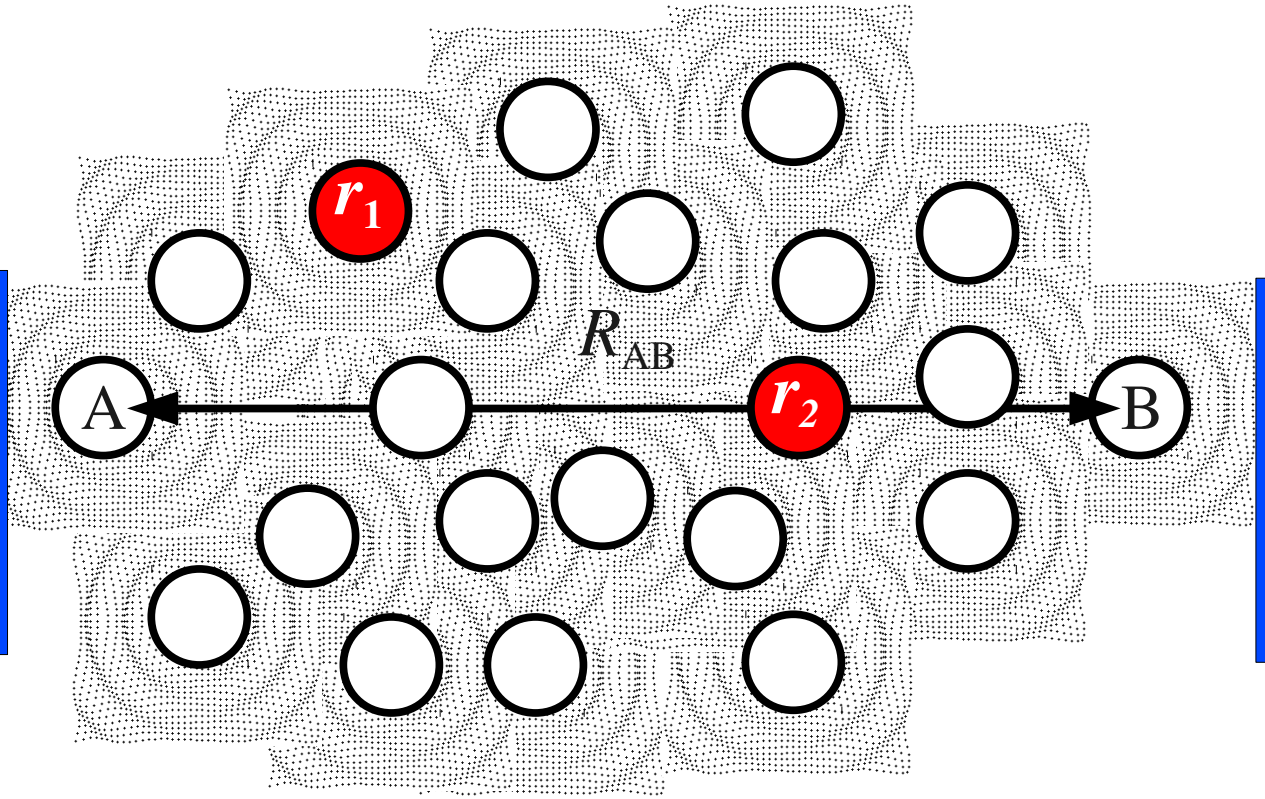


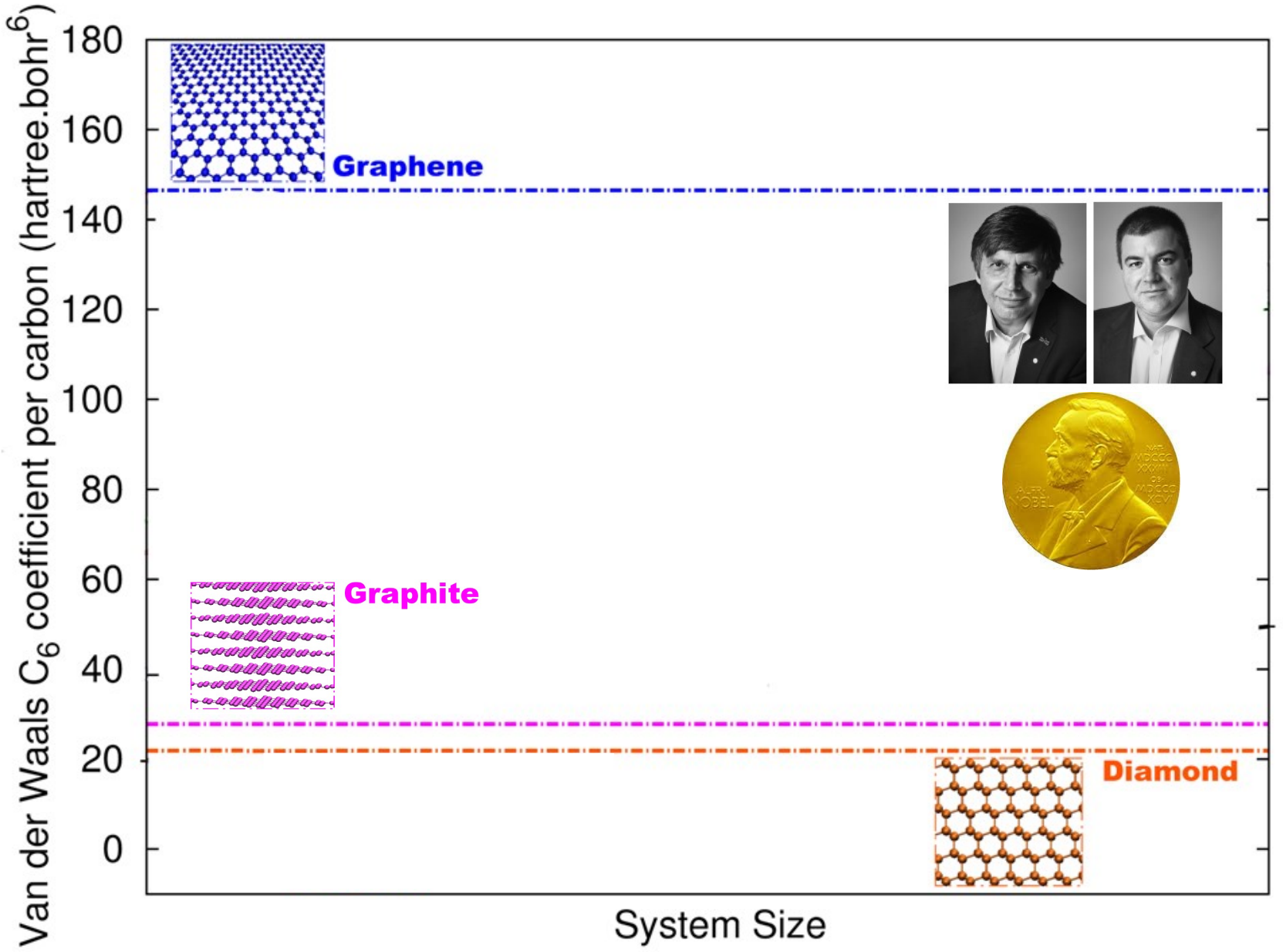
2

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

$$E_c = -\int_0^\infty \frac{d\omega}{2\pi}\int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1},\mathbf{r_2};i\omega)-\chi_0(\mathbf{r_1},\mathbf{r_2};i\omega))\frac{1}{|\mathbf{r_1}-\mathbf{r_2}|}\right)$$

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

Electrodynamic treatment of vdW interactions: beyond "hybridized atoms"



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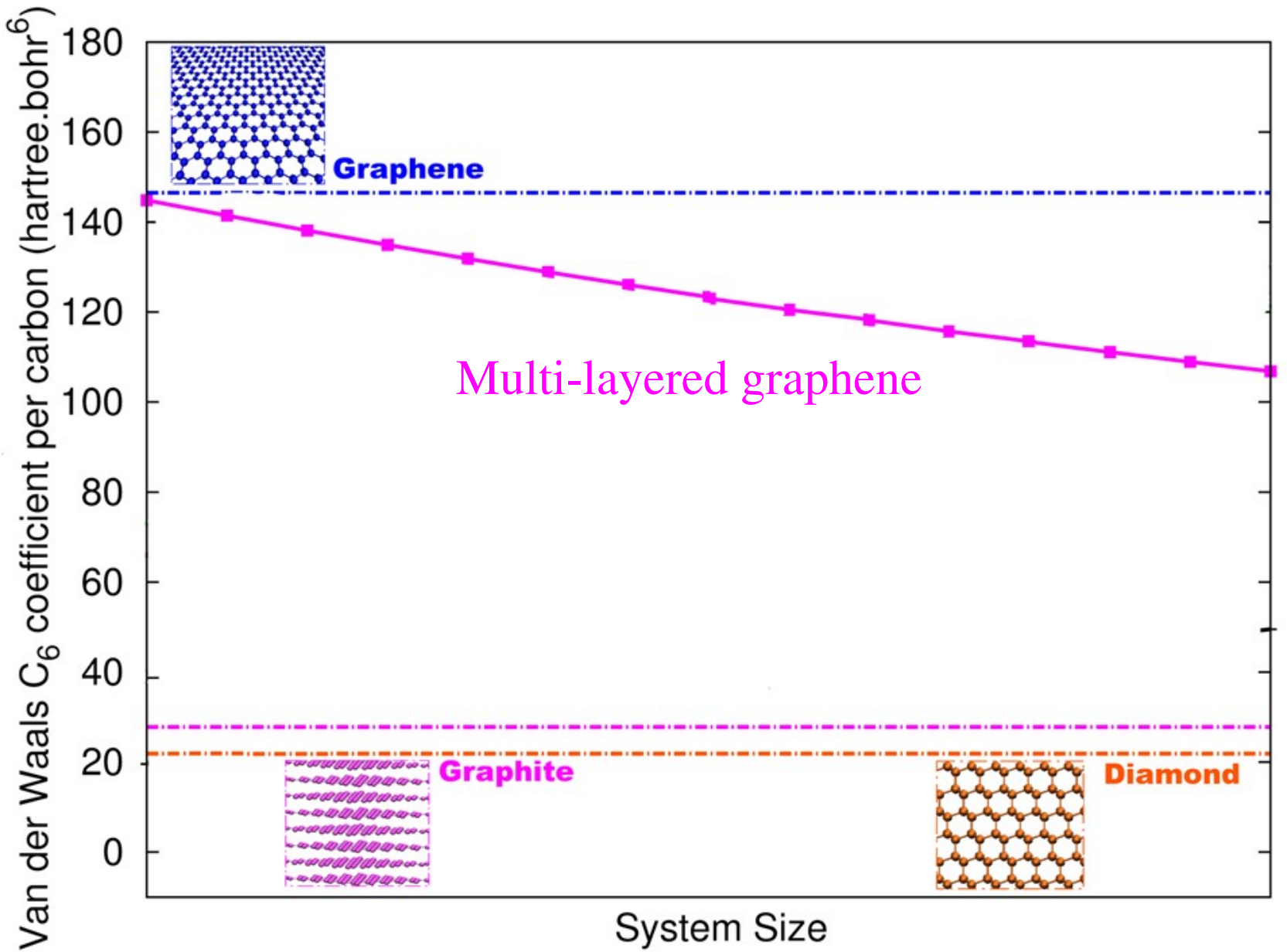

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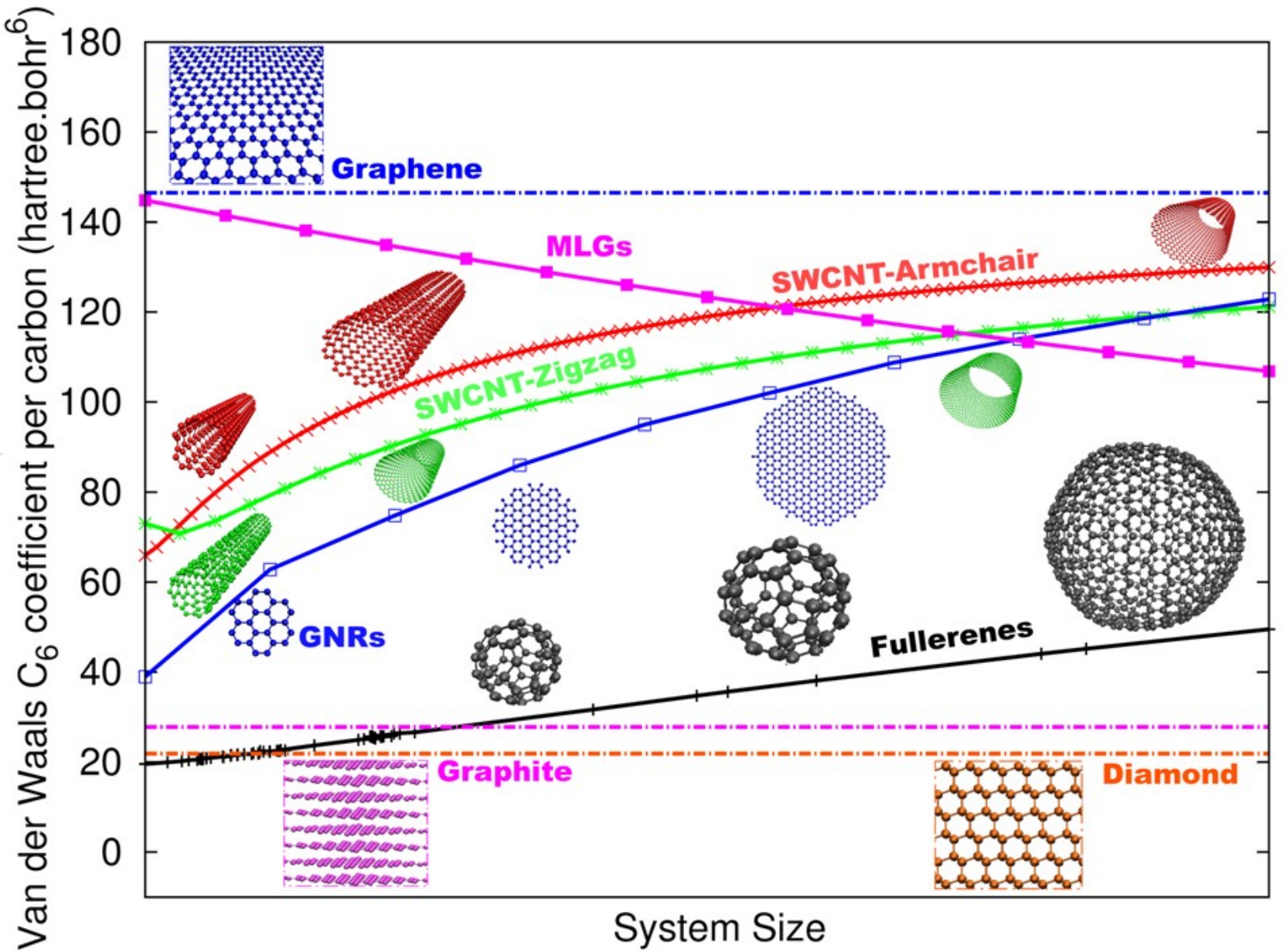

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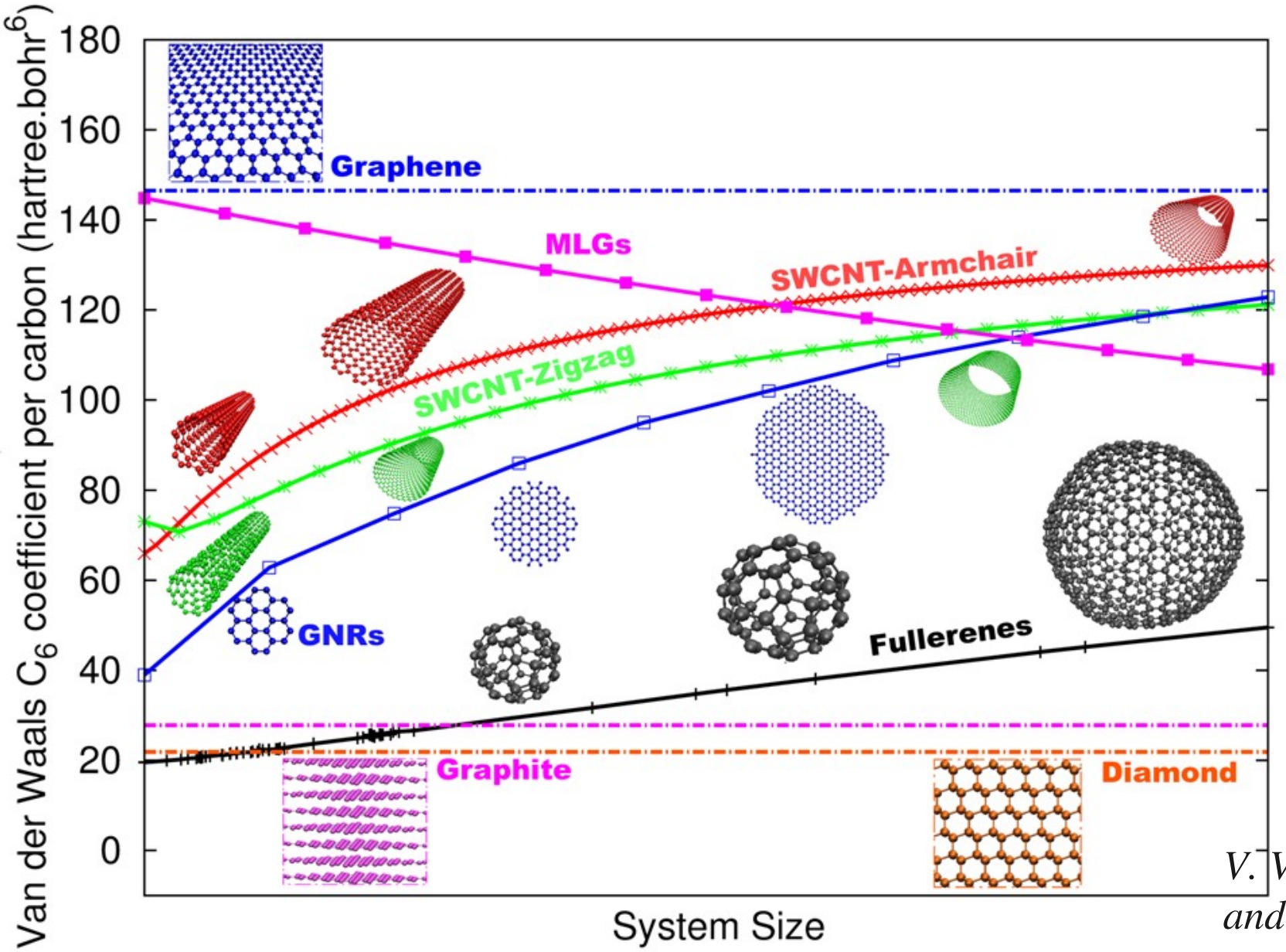
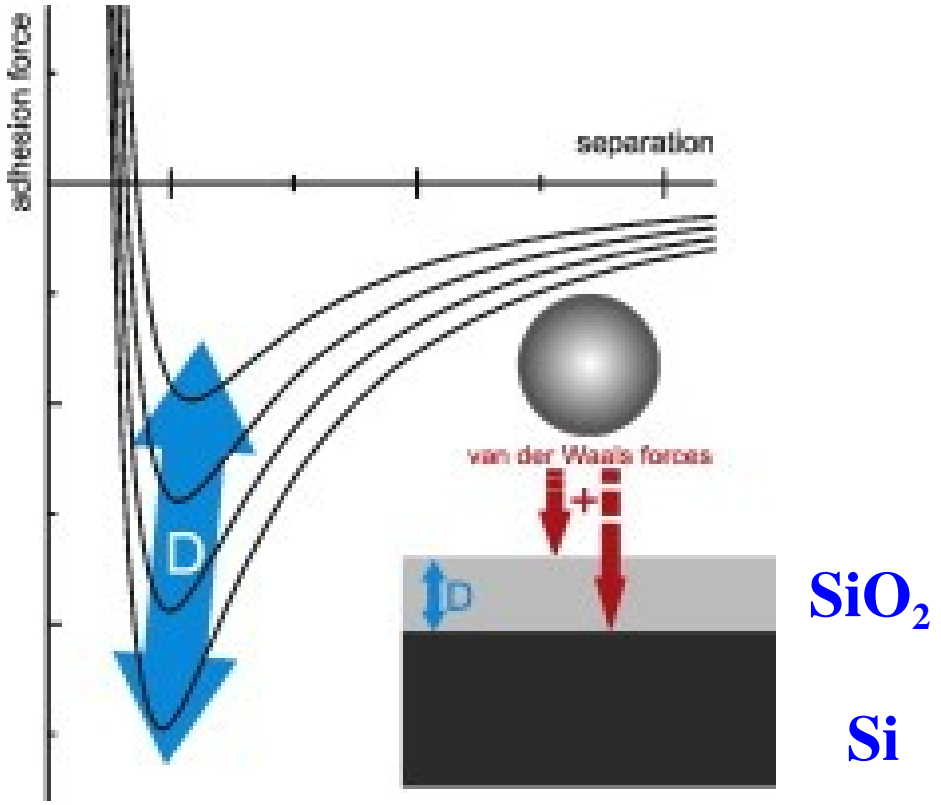


V. V. Gobre and A. Tkatchenko, ***Nature Comm.*** (2013)

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).

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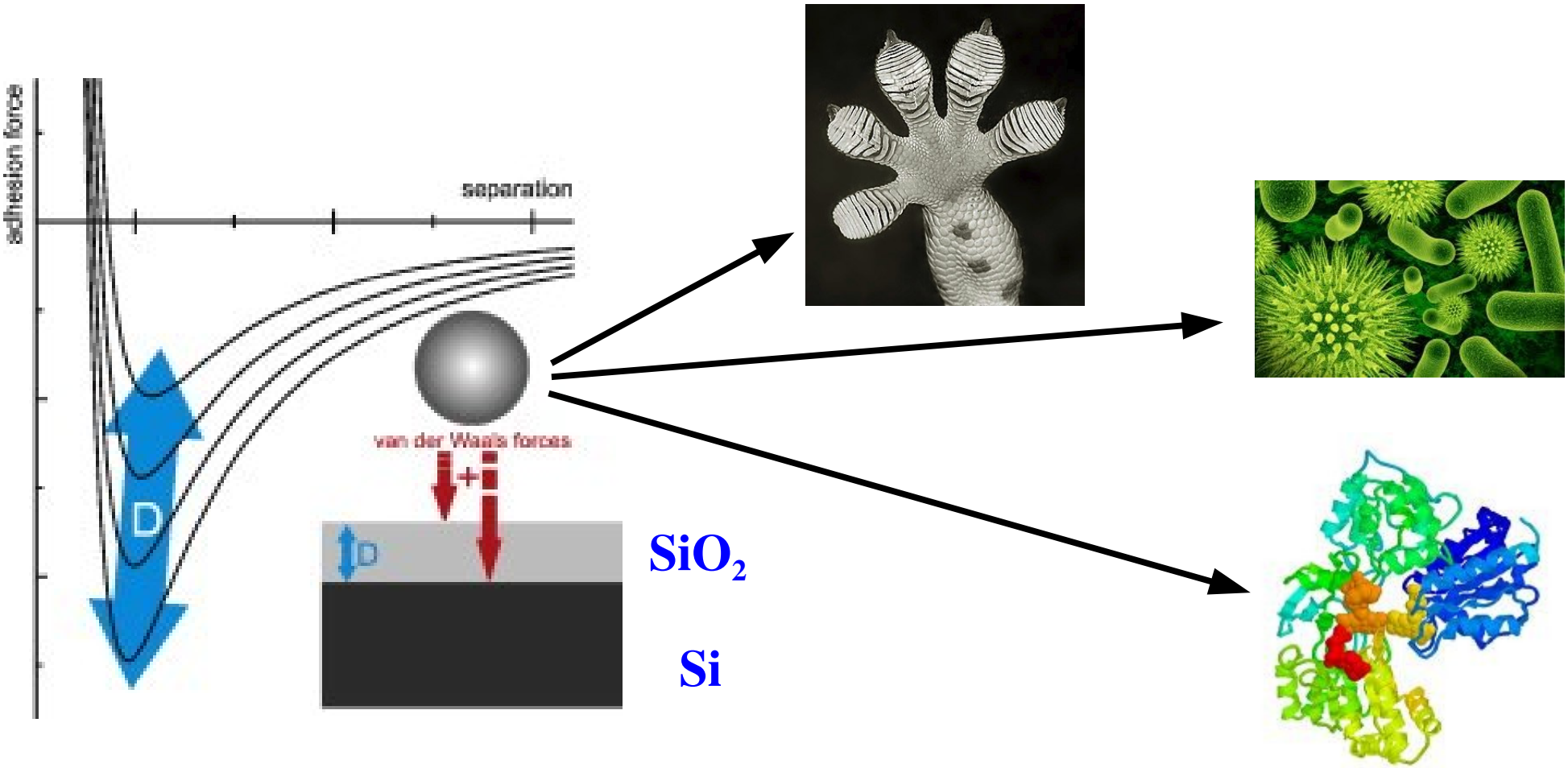

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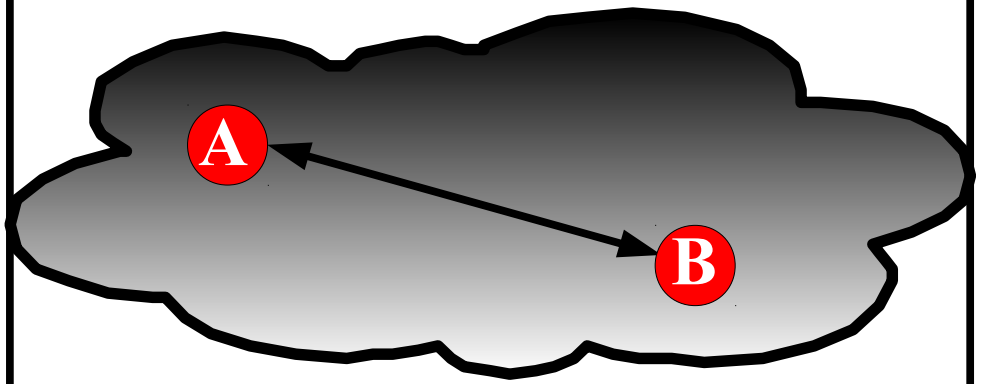
Towards Efficient Many-Body Treatment of vdW Interactions

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

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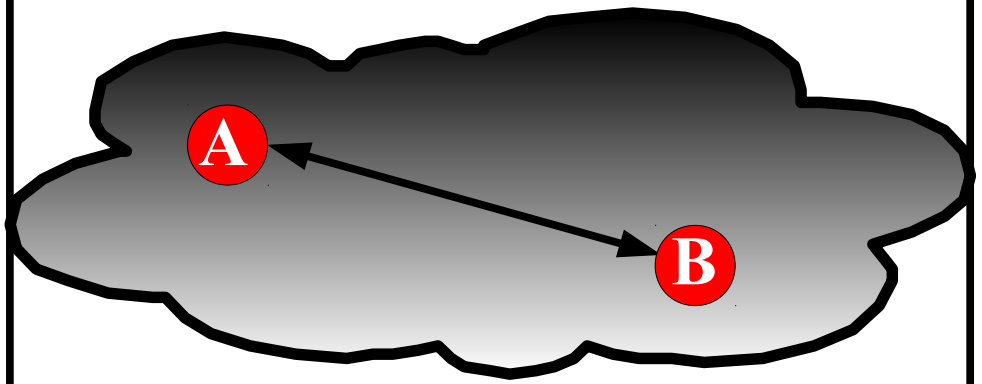
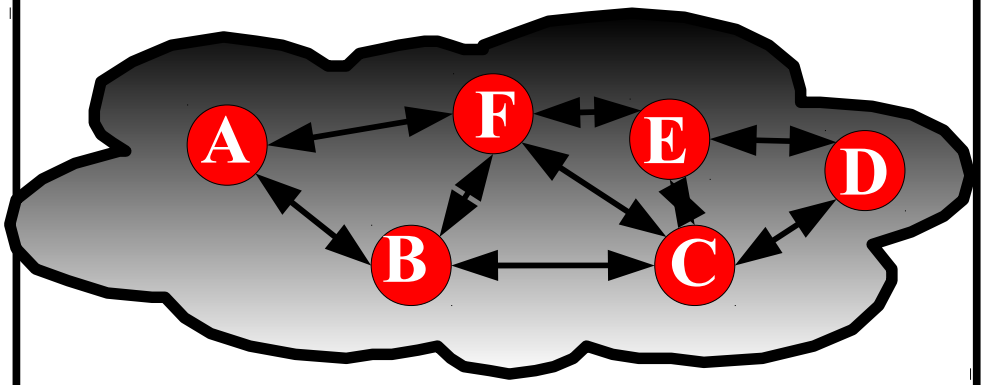


Valid for small molecules ***or*** homogeneous dielectrics

The new state-of-the-art:

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



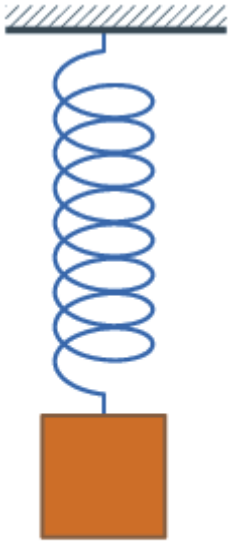
Valid for **small and large molecules, insulators, metals, interfaces, ...**

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)



Nucleus (q)

Harmonic bond (ω)

"Electron" ($-q$,m)

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

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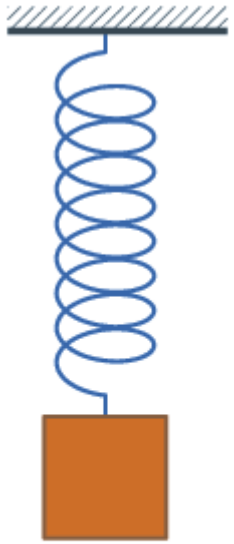

Nucleus (q)

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In the dipole approximation:

(α,ω) fully characterize the QHO

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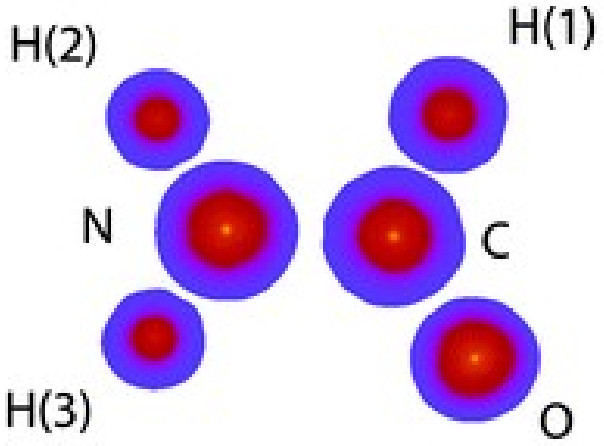
First-Principles Model: QHOs in Molecules and Solids

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



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

$\boldsymbol{\alpha}^0$ and $\boldsymbol{\omega}^0$ include short-range hybridization

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

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)

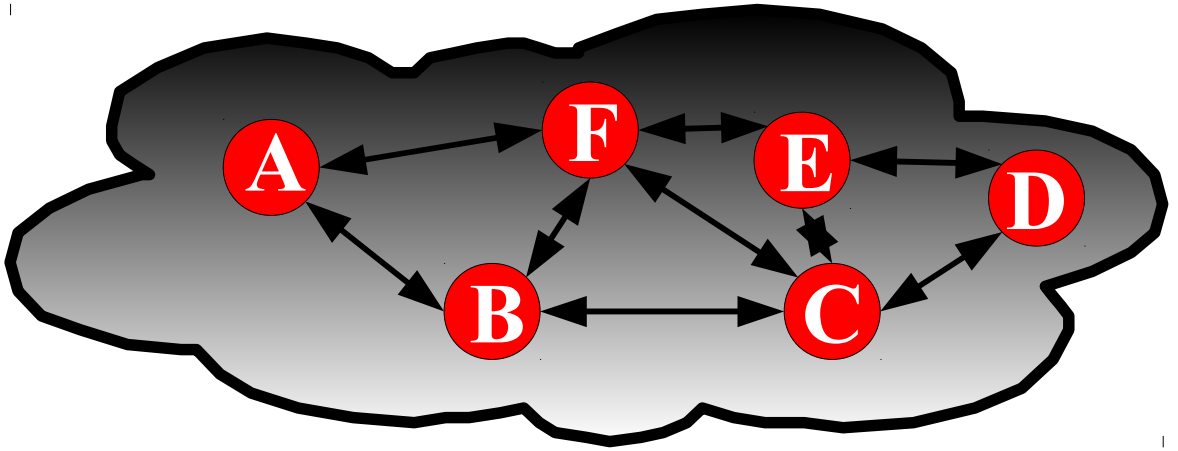
$$\alpha_p(i\omega) = \alpha_p^{\mathrm{TS}}(i\omega) + \alpha_p^{\mathrm{TS}}(i\omega) \sum_{q \neq p}^{N} \mathcal{T}_{pq} \alpha_q(i\omega)$$

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

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

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

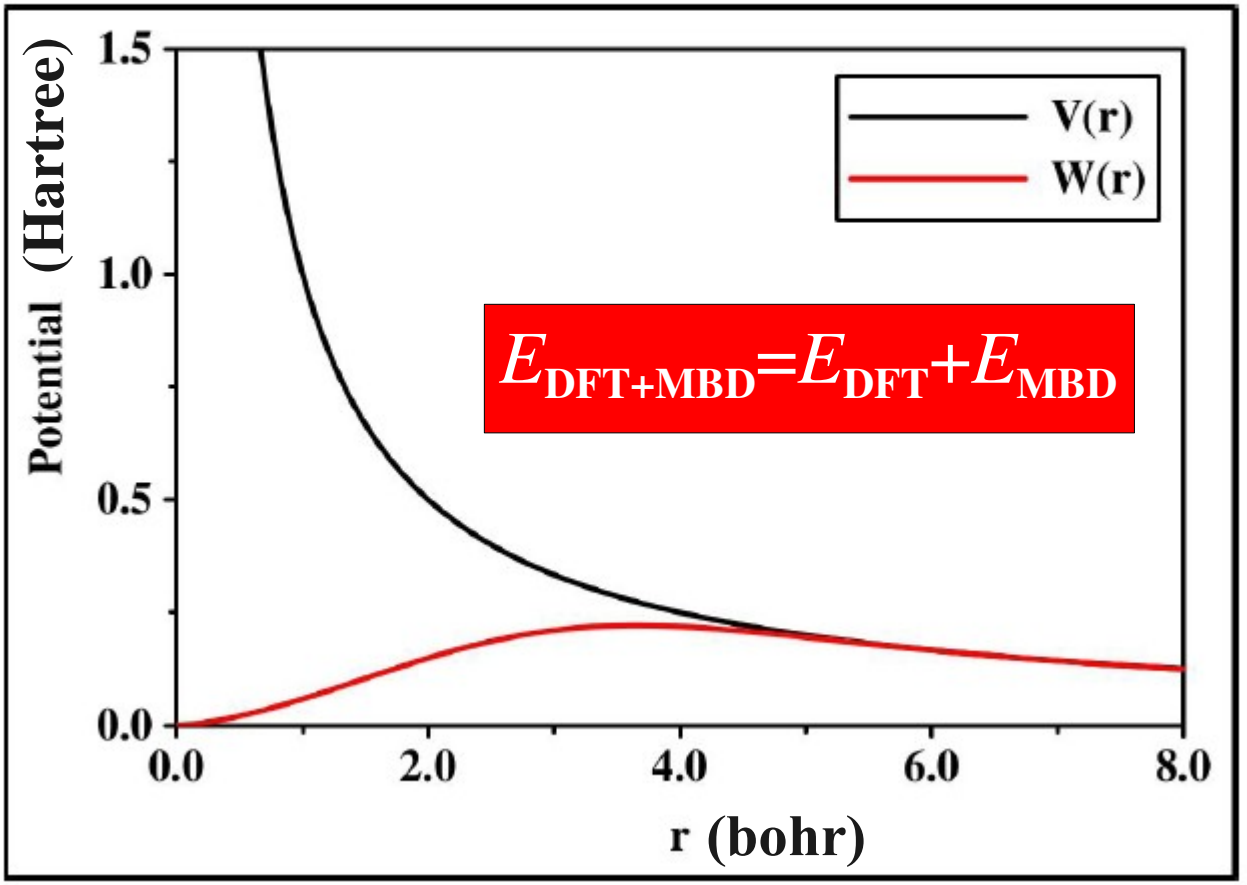
Salient Features of the MBD Method



- 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)

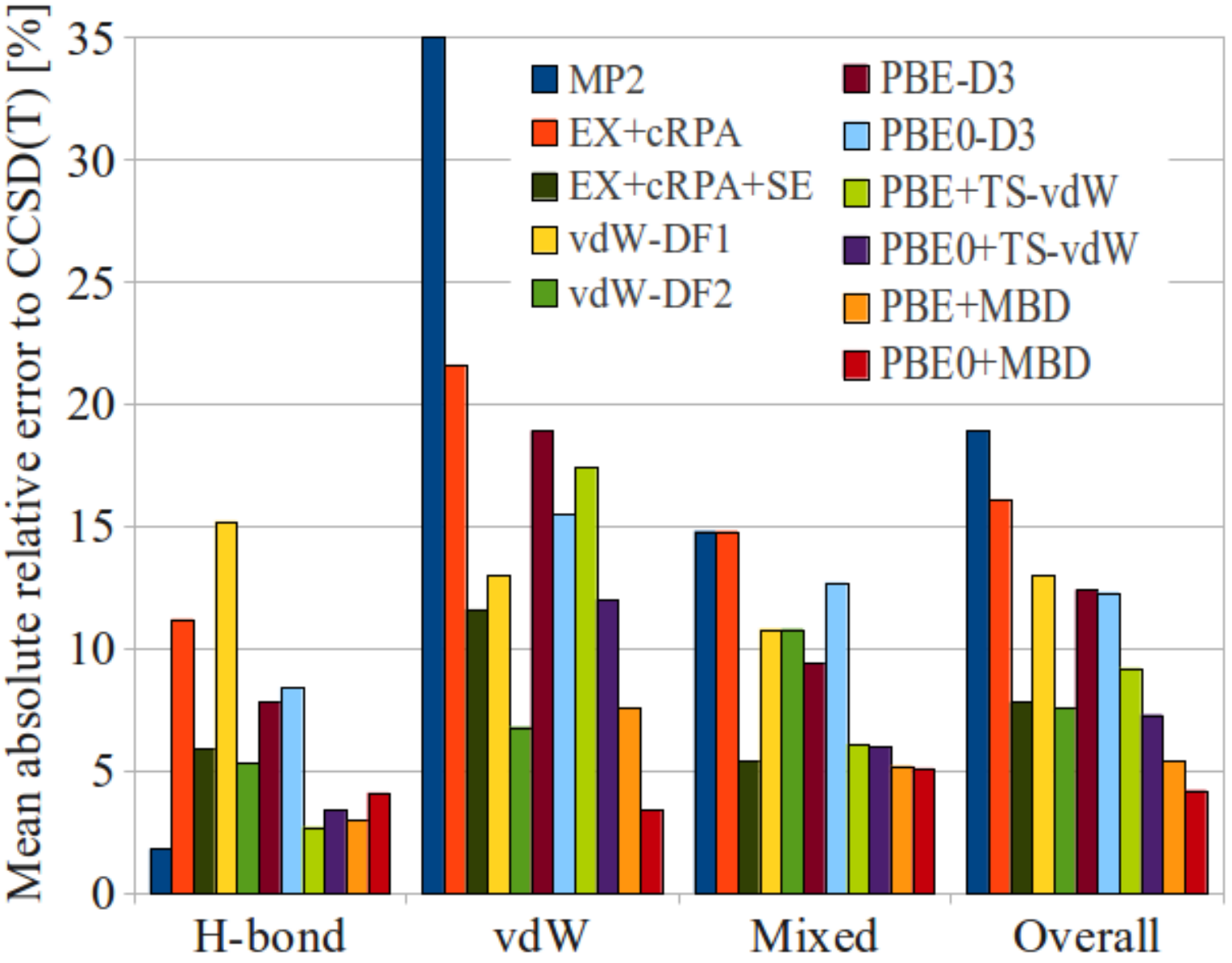
Coupling DFT and MBD by range separation of the Coulomb potential

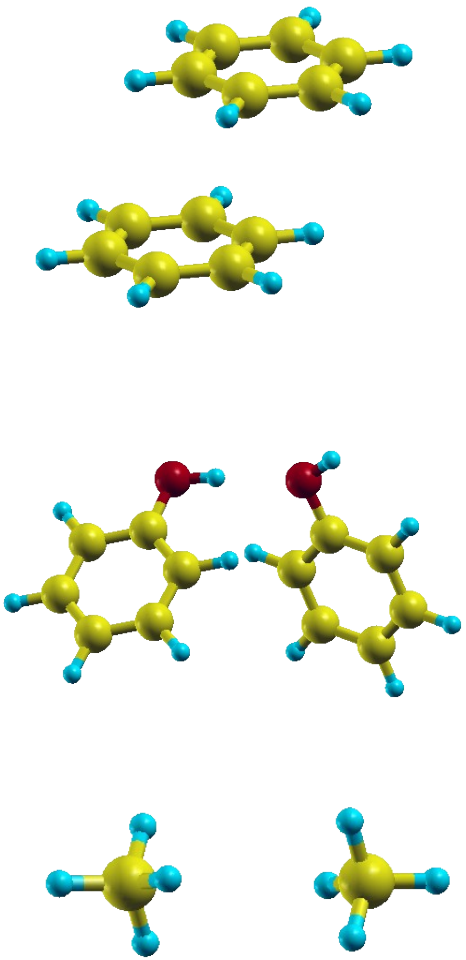
$$W(r_{pq}) = \left(1 - \exp\left(-\left(r_{pq}/R_{pq}^{\mathrm{vdW}}\right)^{\beta}\right)\right)/r_{pq}$$



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

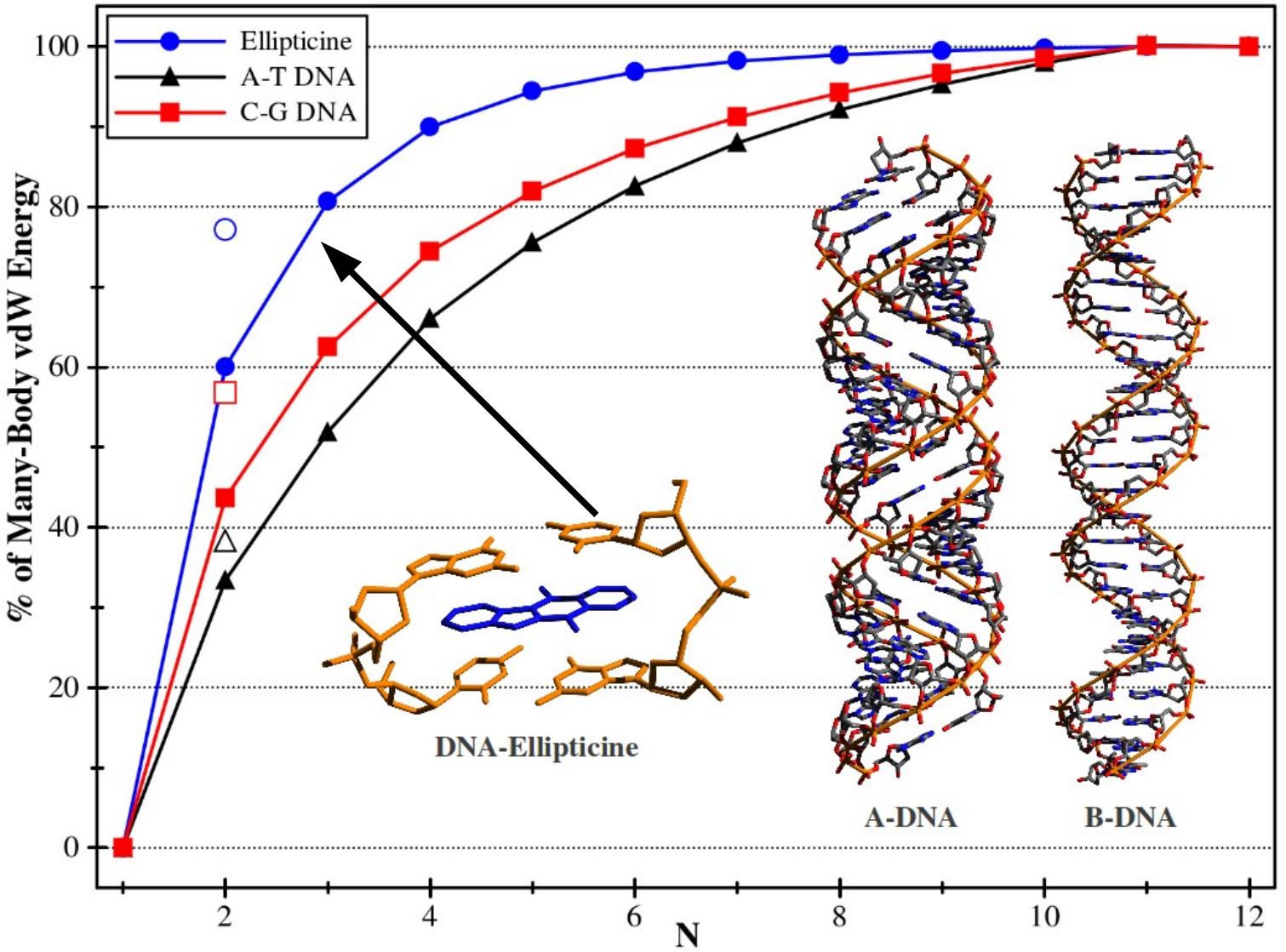
Performance of DFT+MBD for gas-phase intermolecular interactions





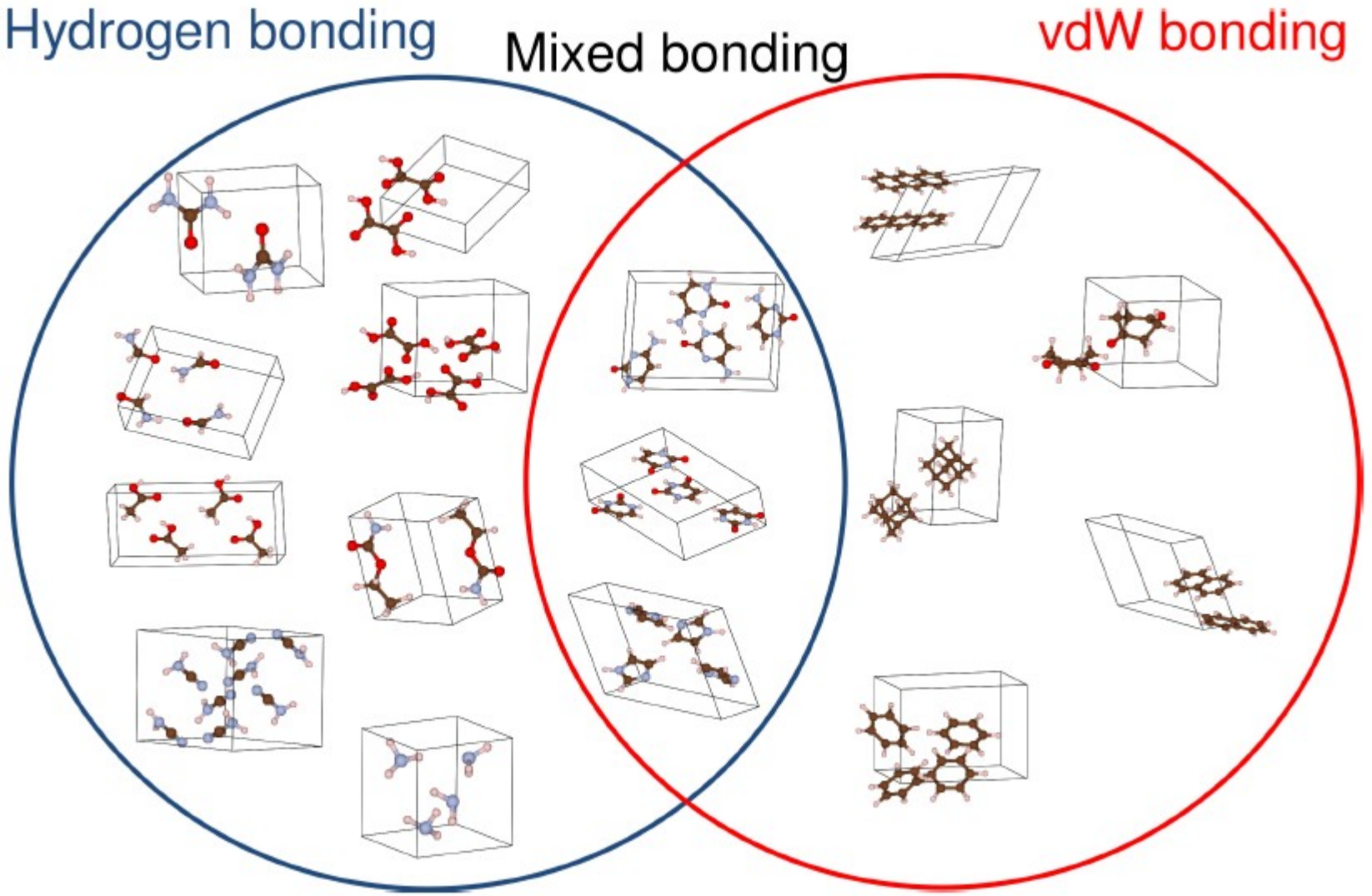
S22 CCSD(T): *Jurecka, Sponer, Cerny, Hobza,* ***PCCP*** (2006); *Sherrill et al.,* ***JCP*** (2010).

Large many-body vdW effects in complex molecular geometries



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

"Chemically Accurate" Predictions for Molecular Materials



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

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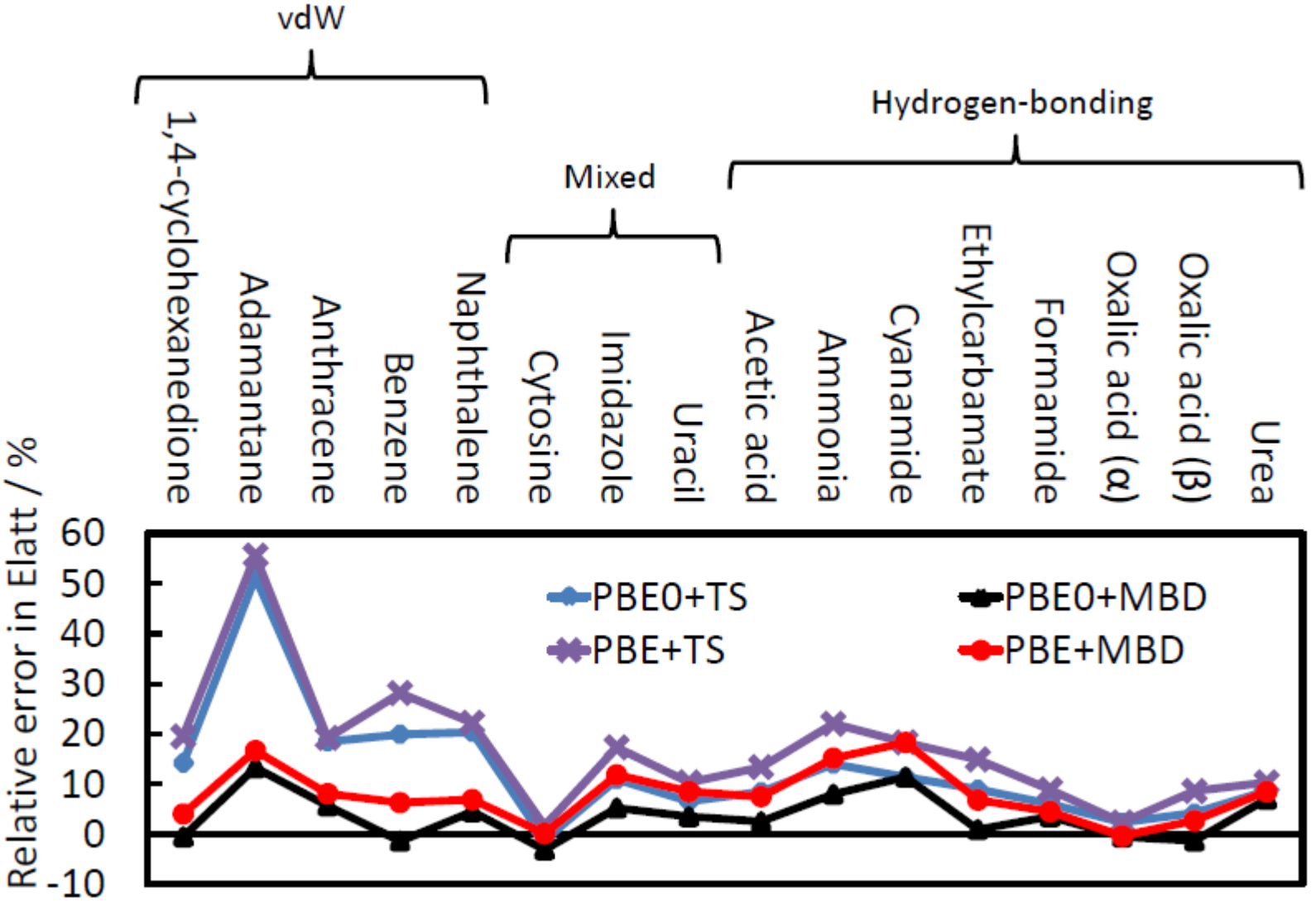

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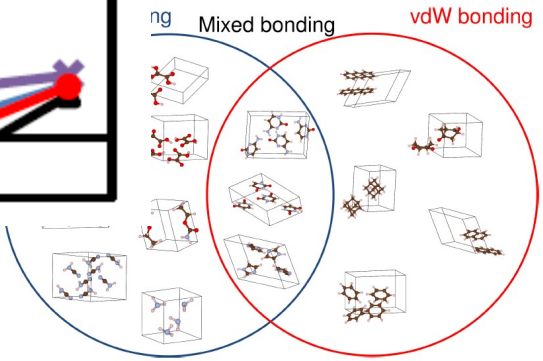
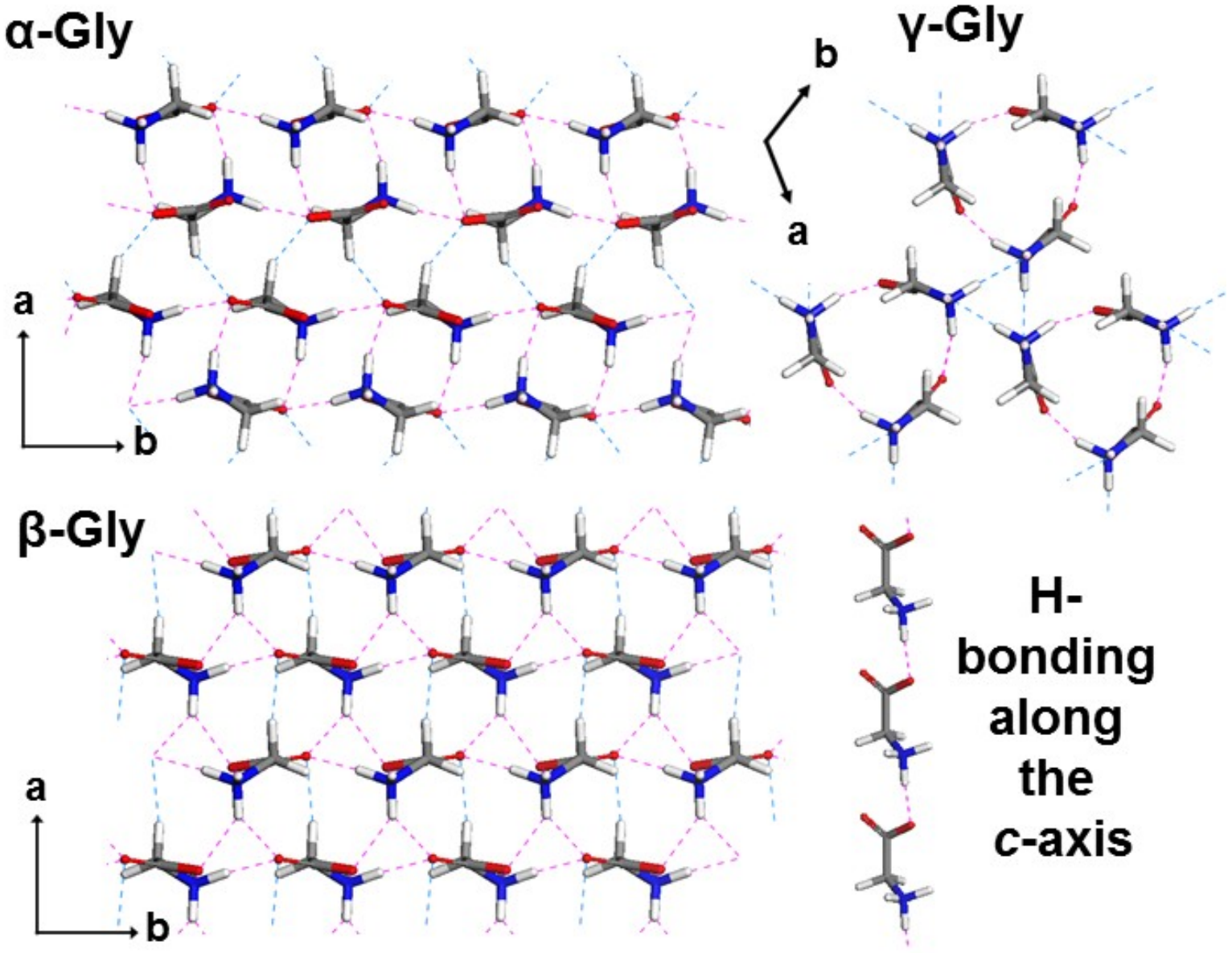


PBE0+MBD overall accuracy: **0.8 kcal/mol; 4.6%**

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

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



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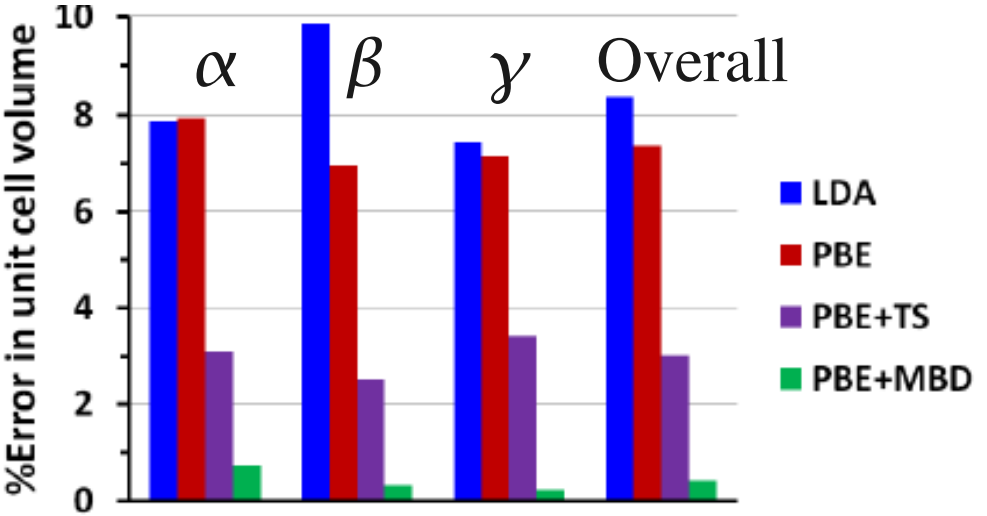
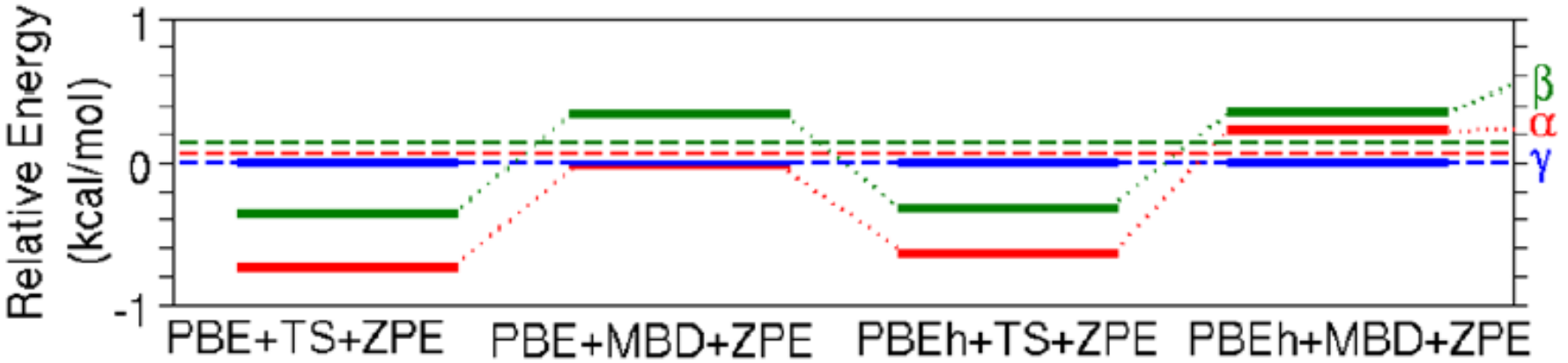
MBD reduces the error in the unit cell volume to less than 0.8%!





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).

Long-range double-screening in DFT+MBD

TS-vdW method

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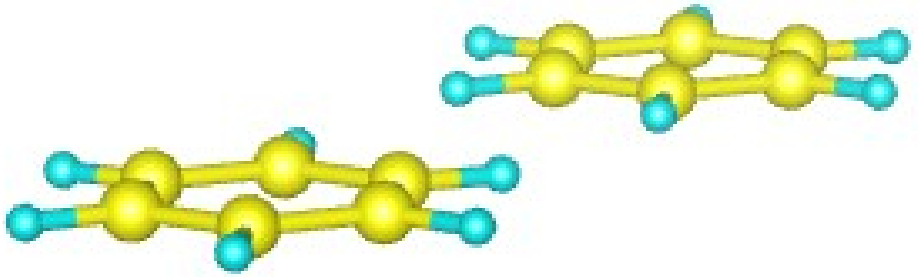
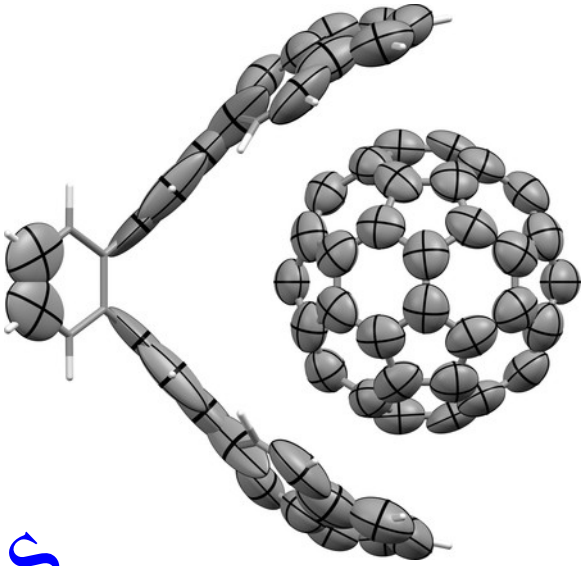
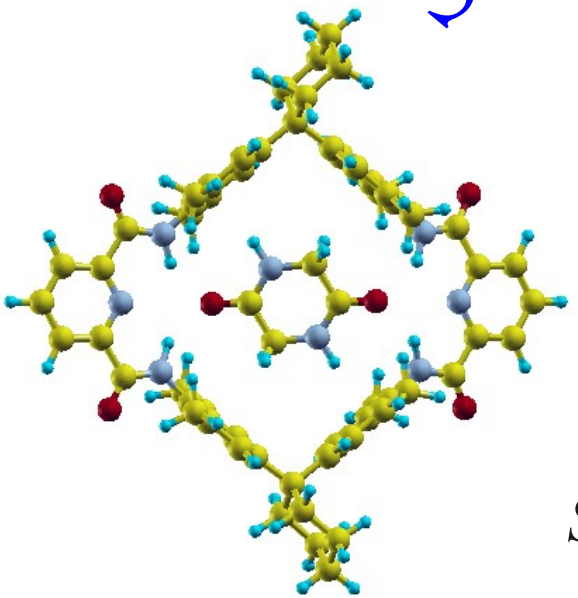
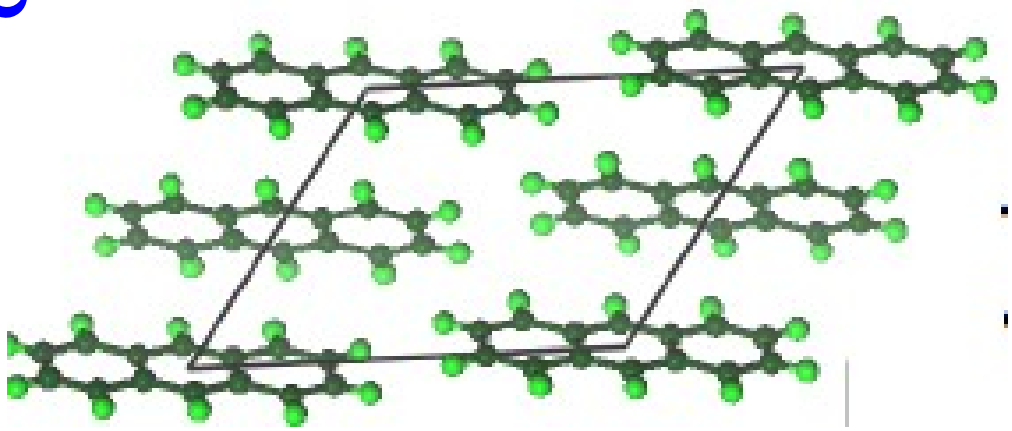




Supramolecular systems: a link between gas-phase molecules and molecular crystals

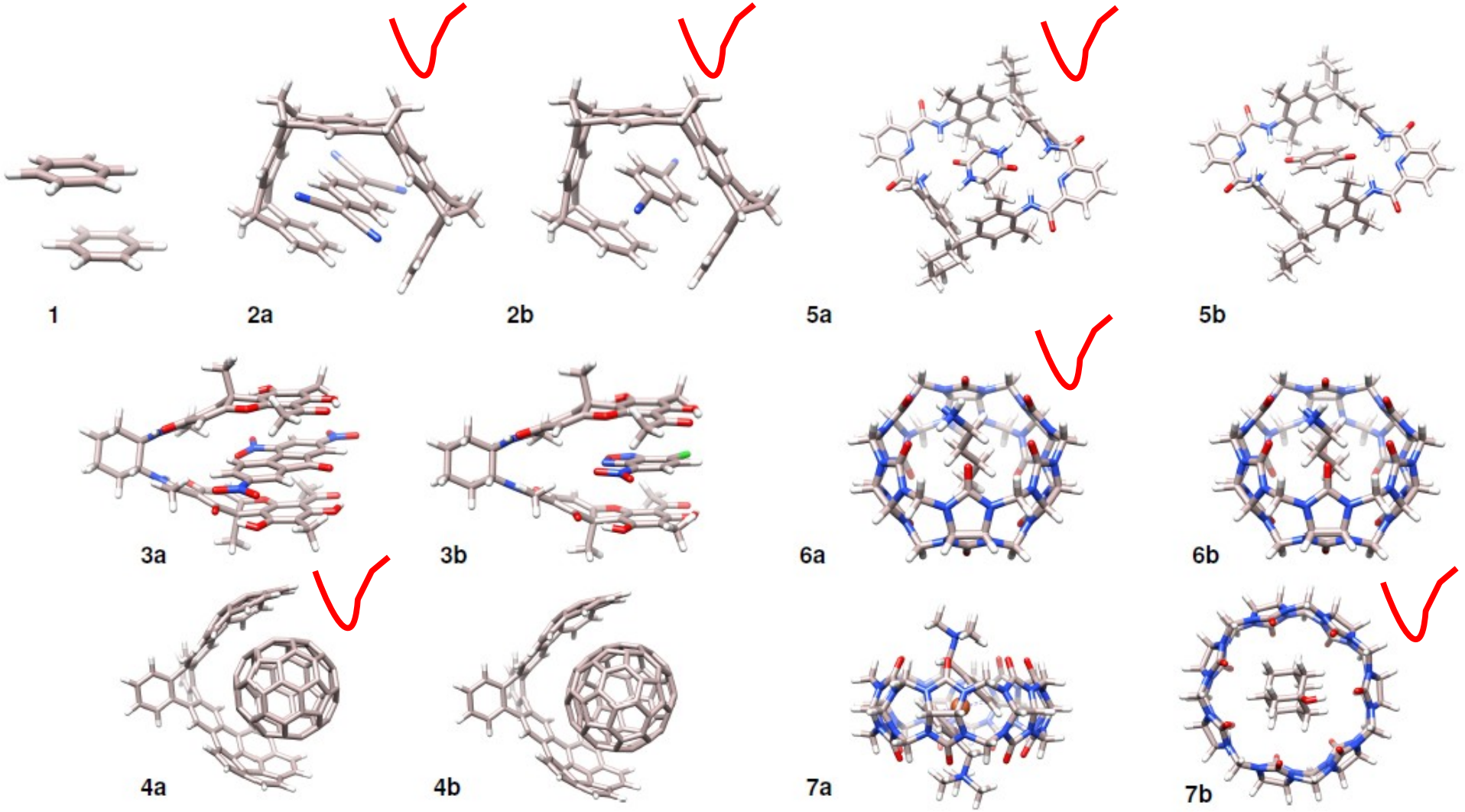




S. Grimme et al., ***JCTC*** (2013).

6 systems out of **S12L** database

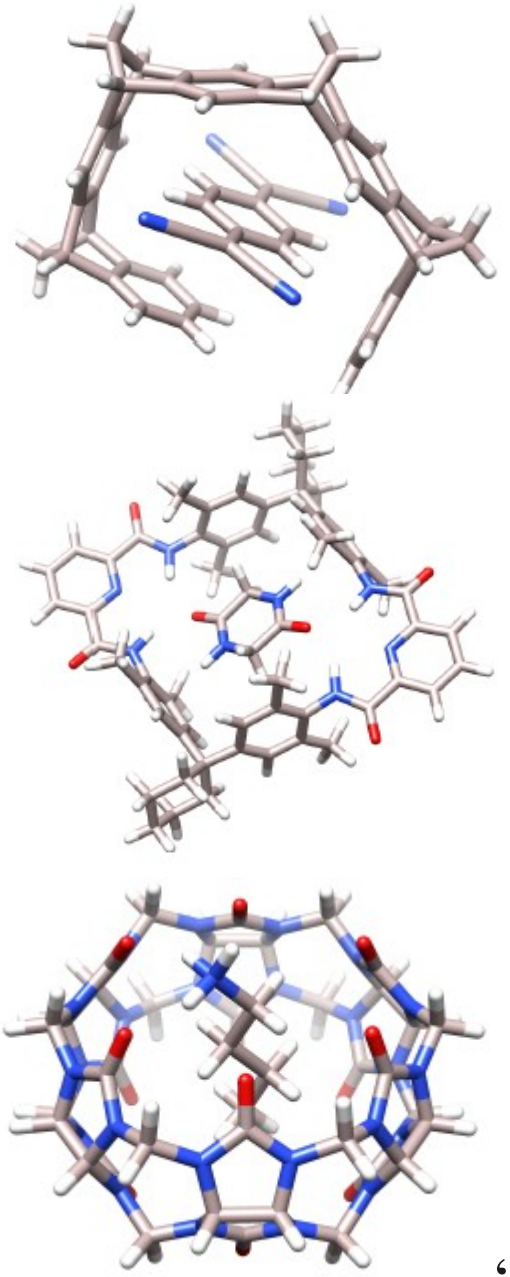
S. Grimme, ***Chem. Eur. J.*** (2012)



Diffusion Quantum Monte Carlo: *A. Tkatchenko, D. Alfe, K. S. Kim*, ***JCTC*** (2012); and *D. Alfe et al.*, to be published.

Binding in supramolecular systems:

DMC vs. "Experiment" vs. PBE+MBD*



DMC	"Experiment"	PBE+MBD*
26.5	29.9	27.7
33.4	34.8	32.6
81.1	77.4	81.6

(**kcal/mol**, DMC sampling error is +/- 1.5 kcal/mol)

"Experimental" values: *S. Grimme*, ***Chem. Eur. J.*** (2012).

Binding in supramolecular systems:

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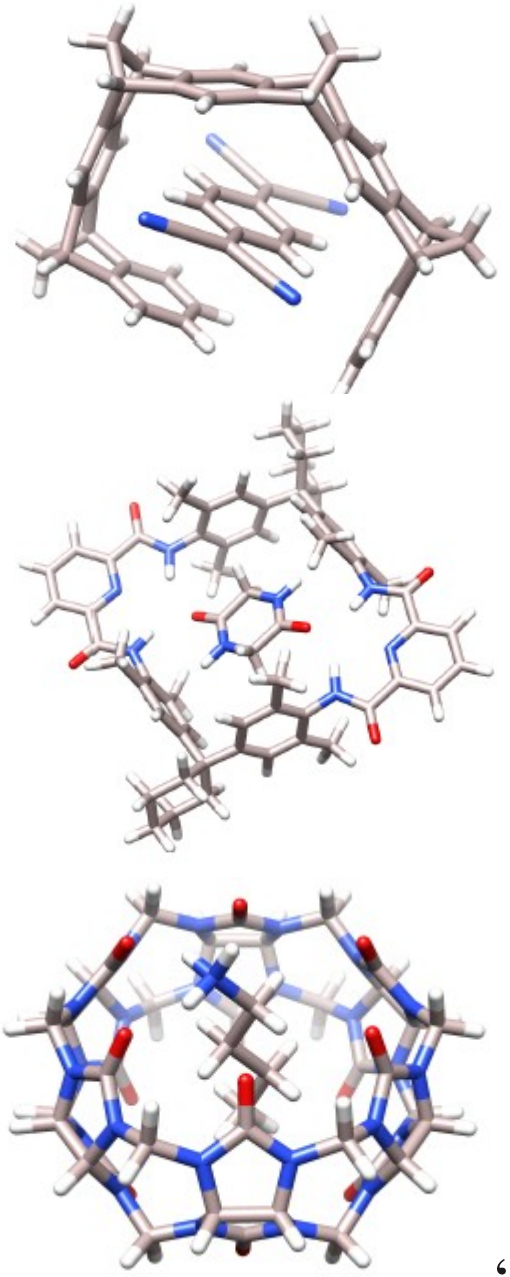

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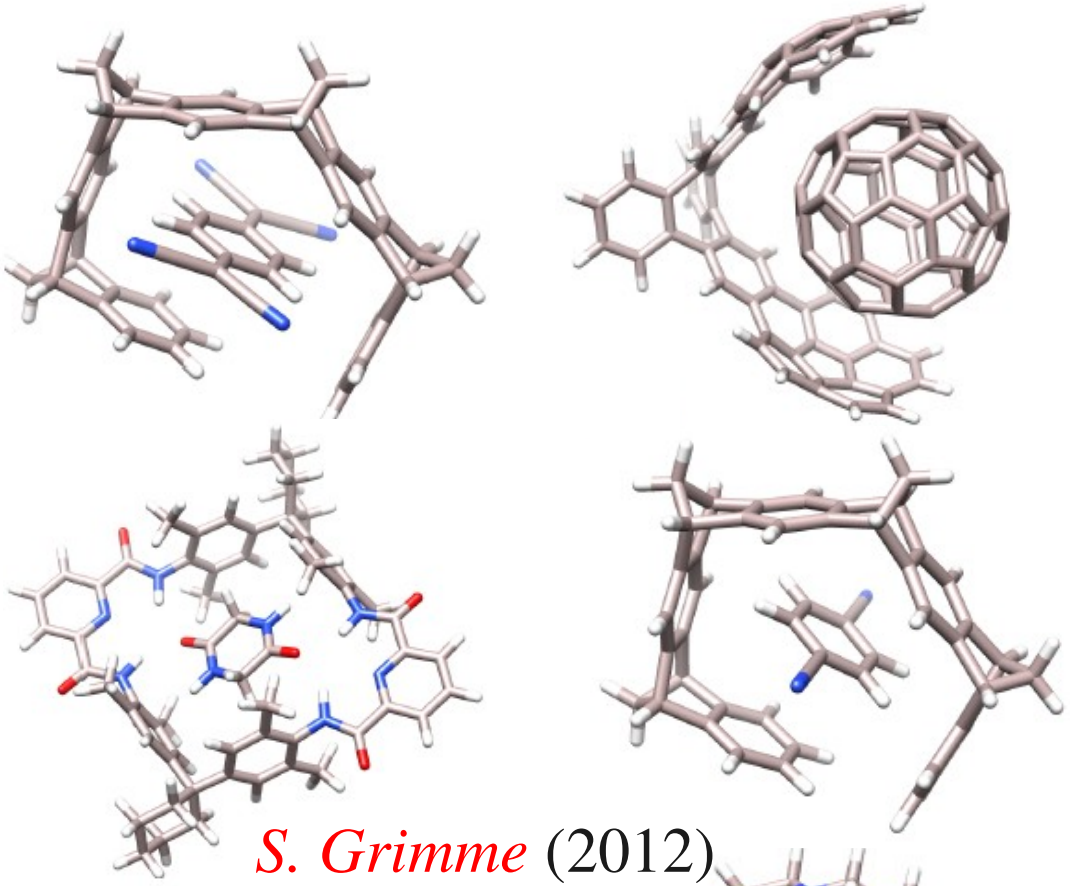
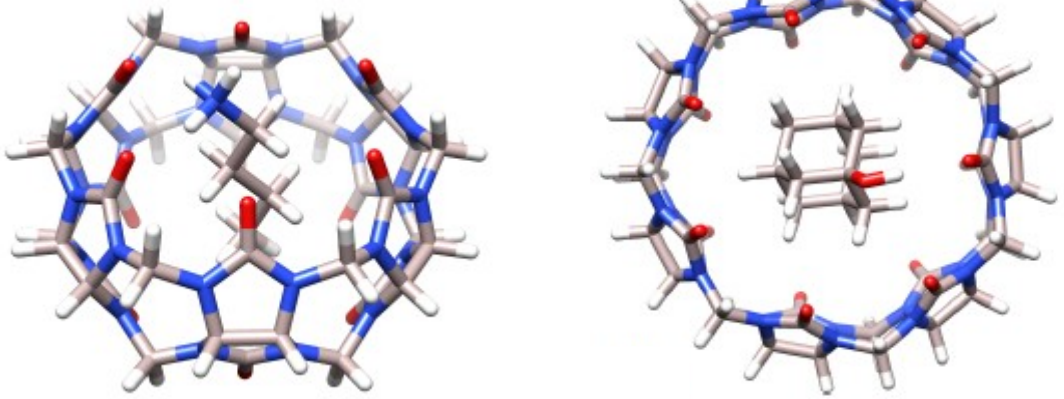
"Experimental" values: *S. Grimme*, ***Chem. Eur. J.*** (2012).

Binding in supramolecular systems: PBE+MBD performance within DMC error bar

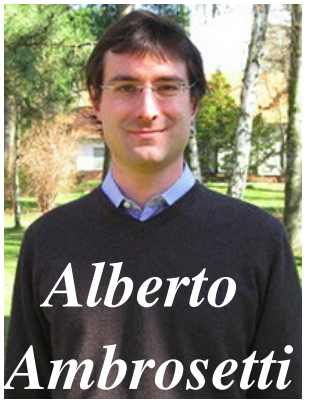


S. Grimme (2012)



MAE of PBE+MBD* vs. DMC:
1.6 kcal/mol

MAE of PBE+MBD* vs. "Exp."
2.9 kcal/mol



Reconciling theory and experiment: Measurement of vdW potential for single adsorbed molecule

PRL **109,** 076102 (2012) PHYSICAL REVIEW LETTERS week ending 17 AUGUST 2012

Measurement of the Binding Energies of the Organic-Metal Perylene-Teracarboxylic-Dianhydride/Au(111) Bonds by Molecular Manipulation Using an Atomic Force Microscope

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[1]*Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany*

[2]*Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany*

(Received 14 March 2012; published 16 August 2012)

to be published, *Phys. Rev. Lett.* (2013)

Adsorption geometry determination of single molecules by atomic force microscopy

Bruno Schuler,[1,*] Wei Liu,[2] Alexandre Tkatchenko,[2] Nikolaj Moll,[1]
Gerhard Meyer,[1] Anish Mistry,[3] David Fox,[3] and Leo Gross[1]

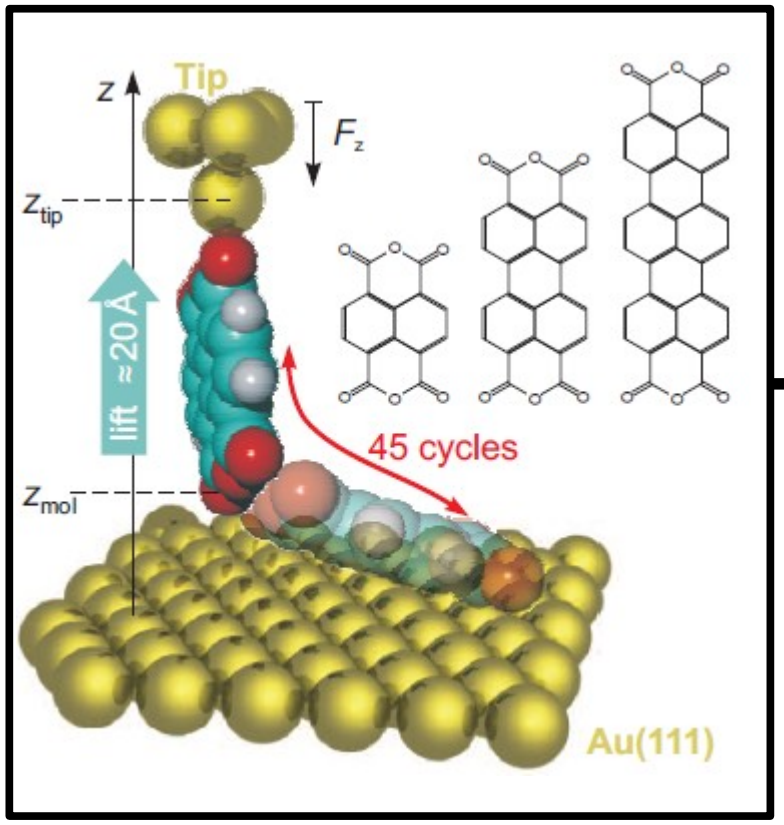
[1]*IBM Research – Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland*

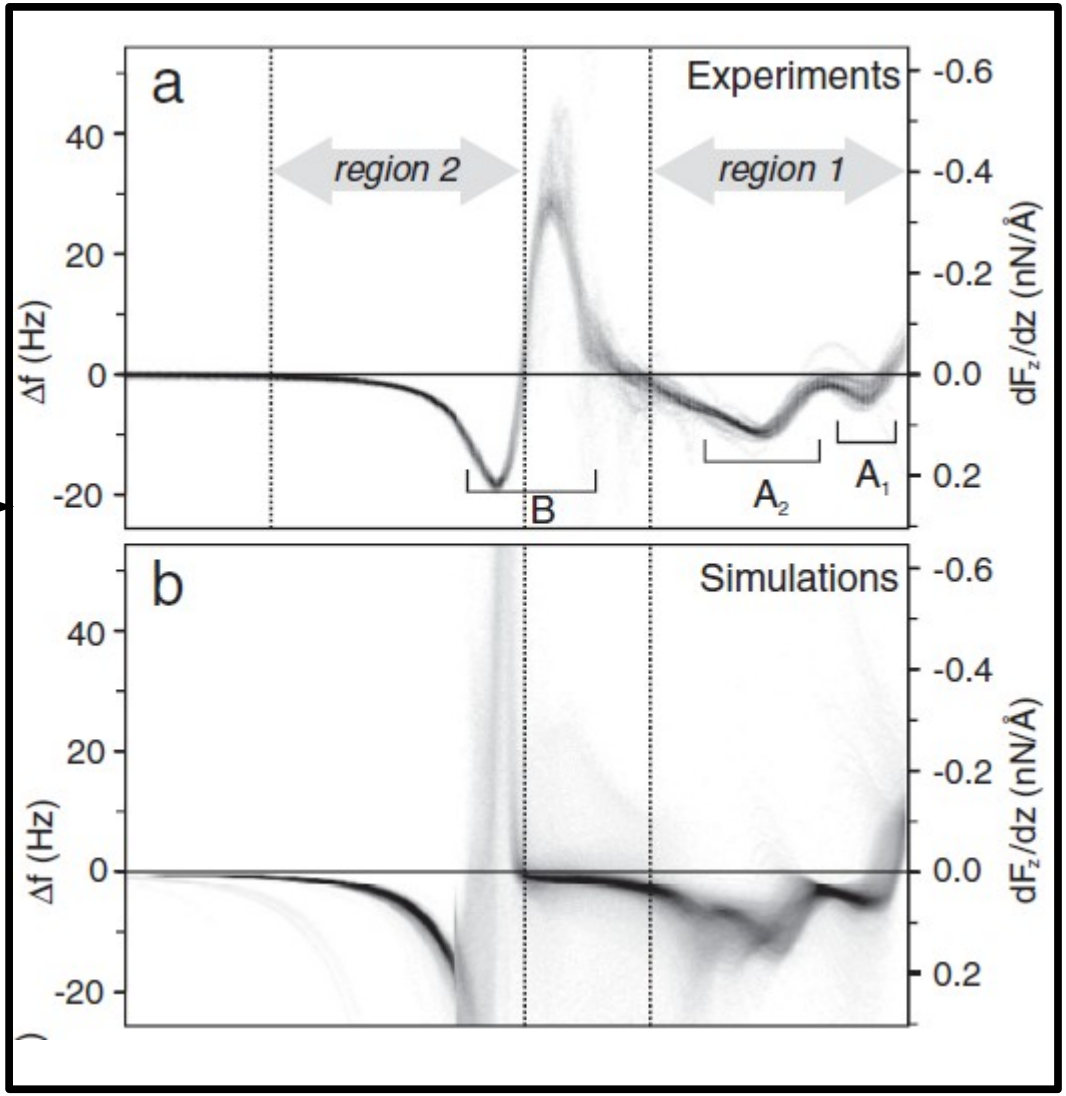
[2]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

[3]*University of Warwick, Gibbet Hill, CV34 Warwick, UK*

(Dated: July 2, 2013)

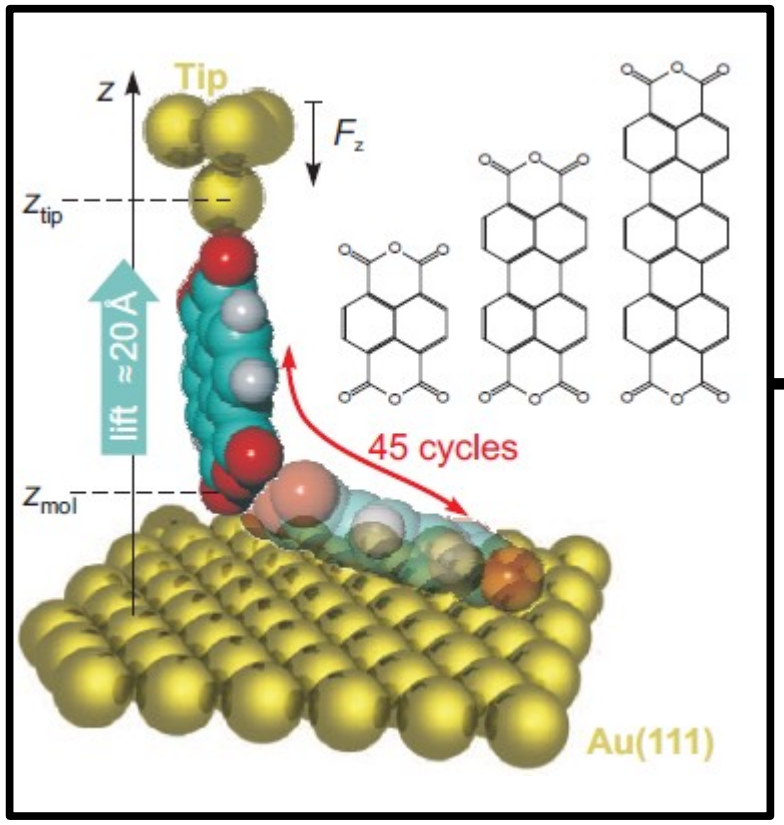
Single-molecule measurement of adsorption energy by AFM

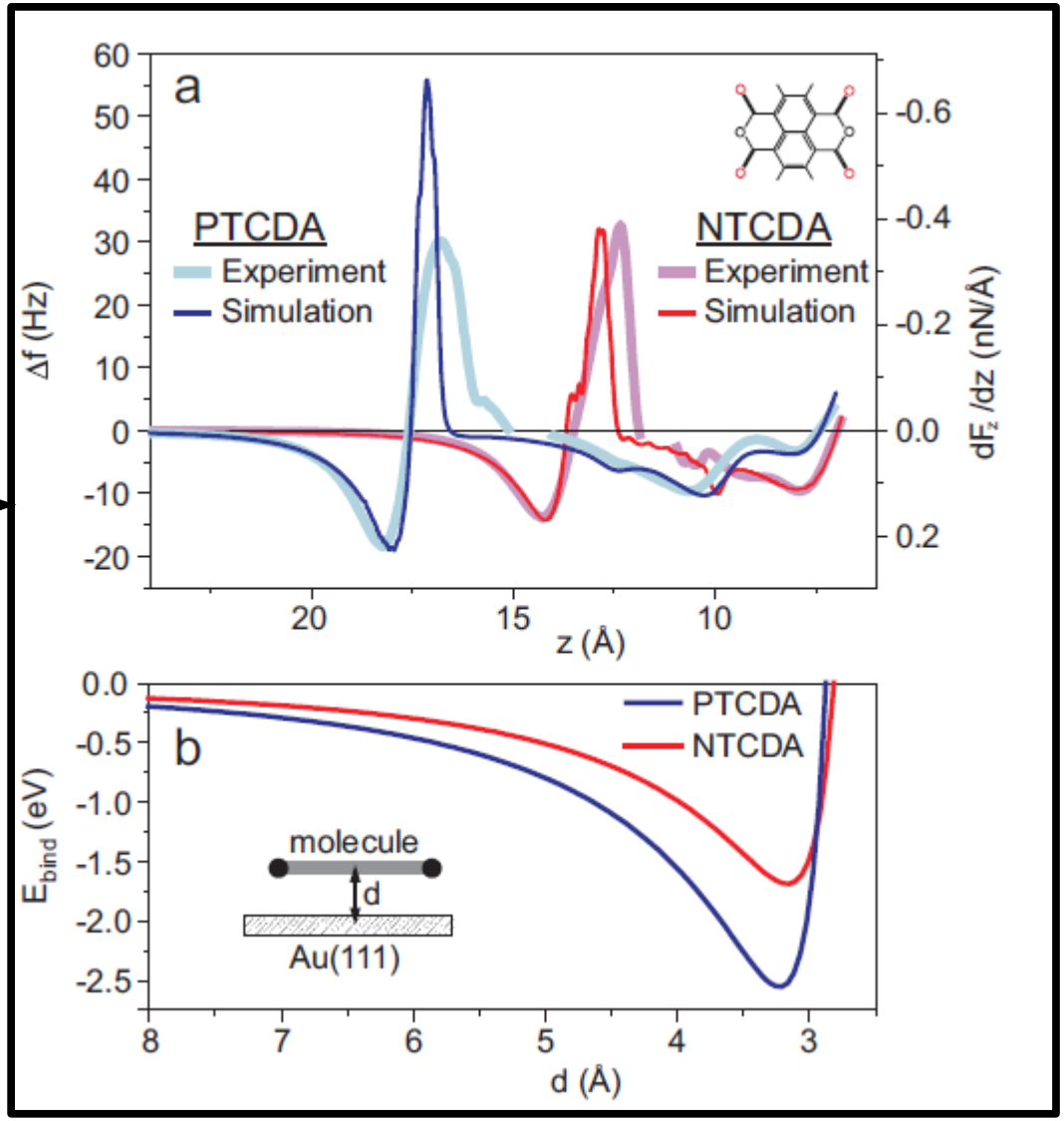




C. Wagner *et al.*,
PRL 109, 076102 (2012).

Single-molecule measurement of adsorption energy by AFM

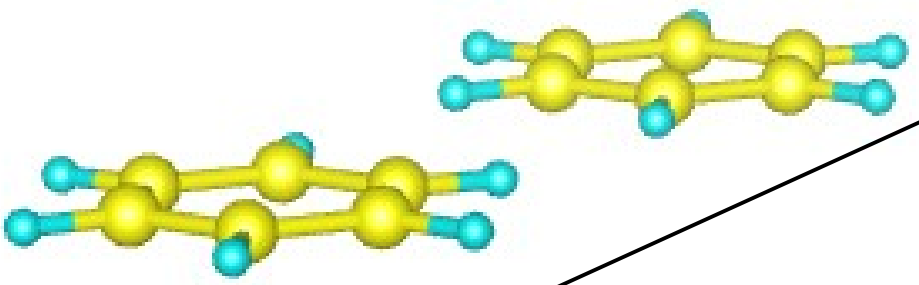




C. Wagner *et al.*,
PRL 109, 076102 (2012).

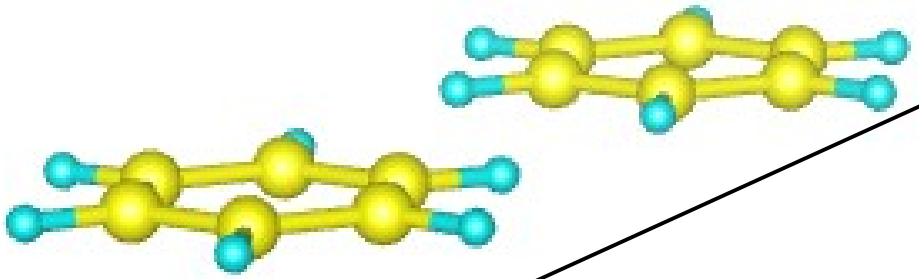
Summary

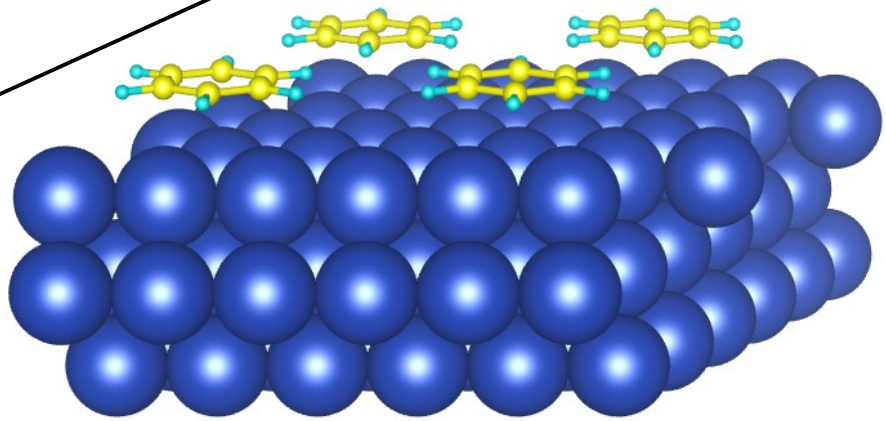
$$C_{6,\mathrm{eff}}^{ii} = C_{6,\mathrm{eff}}^{ii}[n(\mathbf{r})]$$

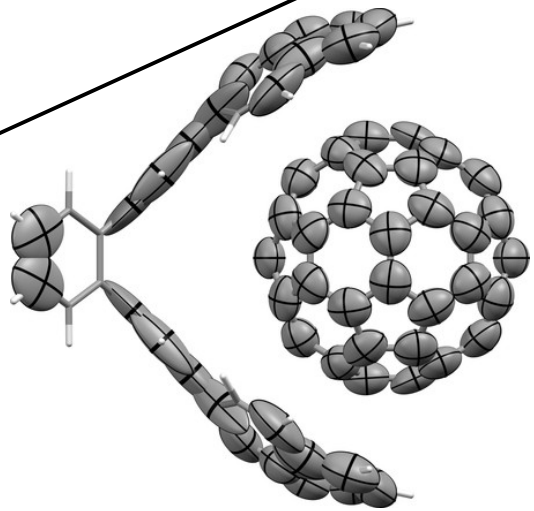


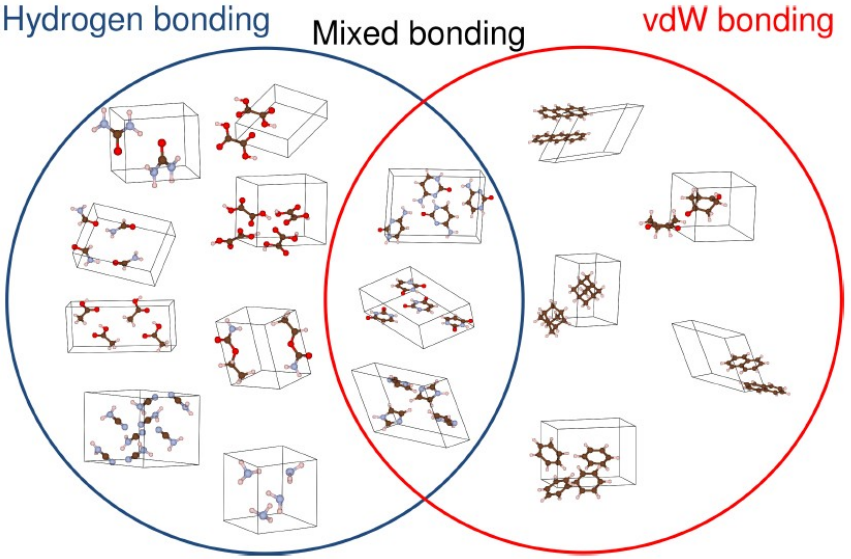
Summary

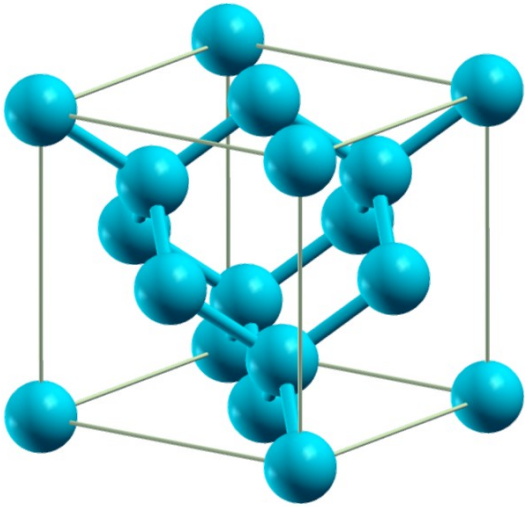
$$C_{6,\mathrm{eff}}^{ii} = C_{6,\mathrm{eff}}^{ii}[n(\mathbf{r})]$$







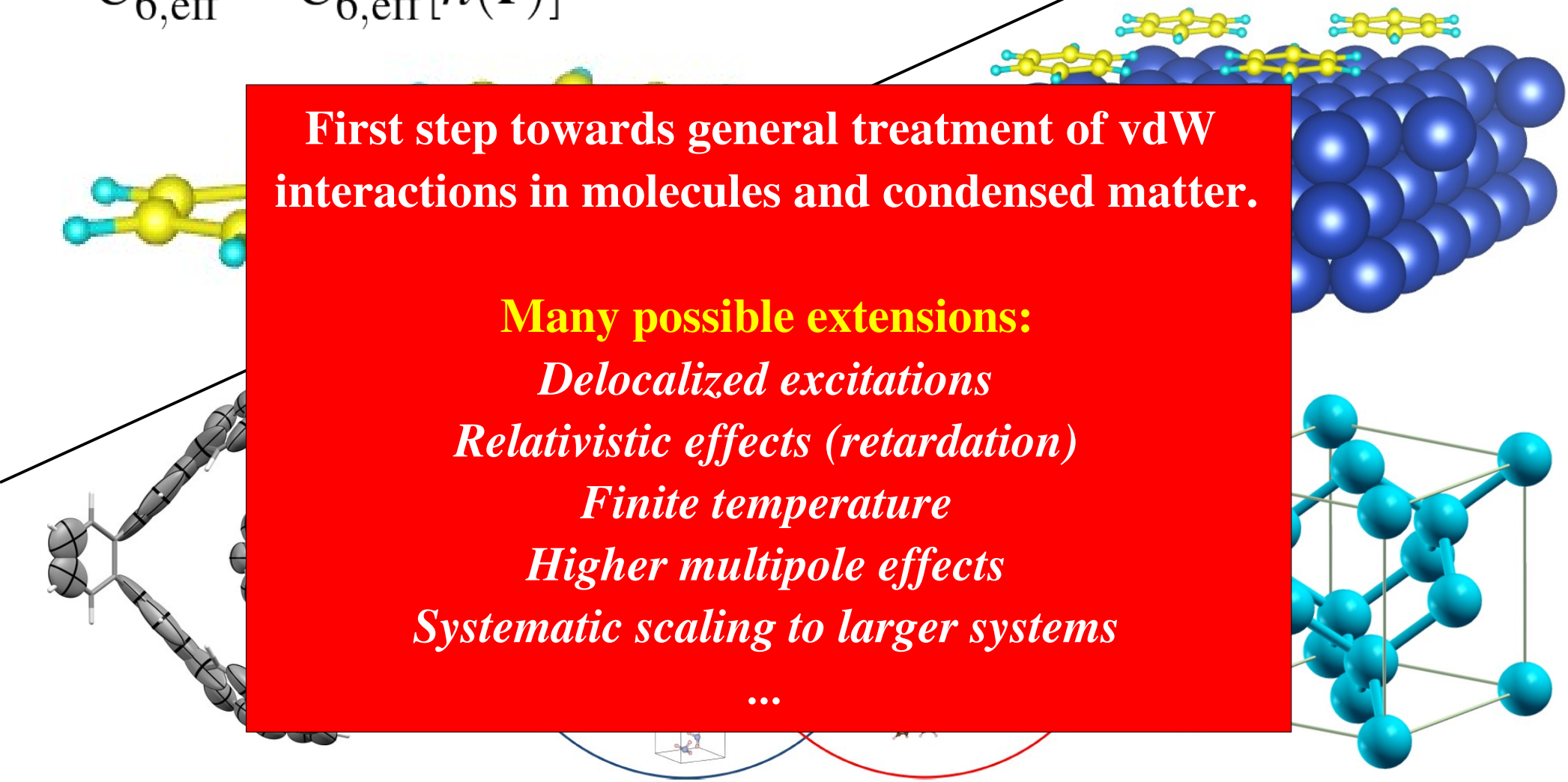




$$E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1}, \mathbf{r_2}; i\omega) - \chi_0(\mathbf{r_1}, \mathbf{r_2}; i\omega)) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \right)$$

Summary

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



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

...

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