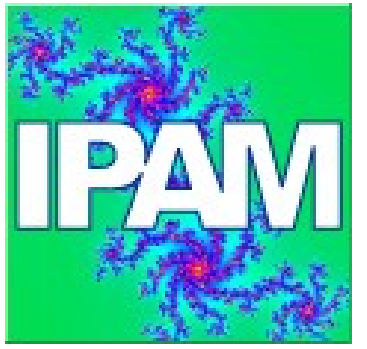


Practical Approaches to Non-Covalent van der Waals Interactions

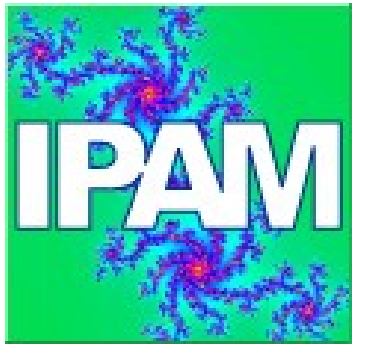
Alexandre Tkatchenko

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

Berlin, Germany

www.fhi-berlin.mpg.de/~tkatchen

IPAM@UCLA, July 24, 2014



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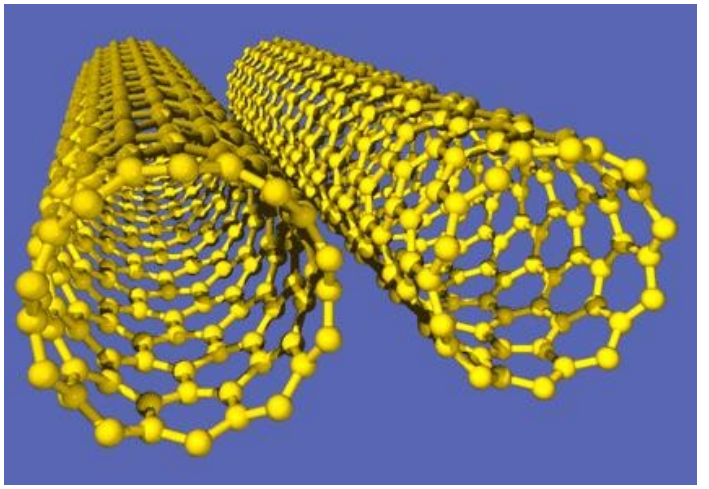
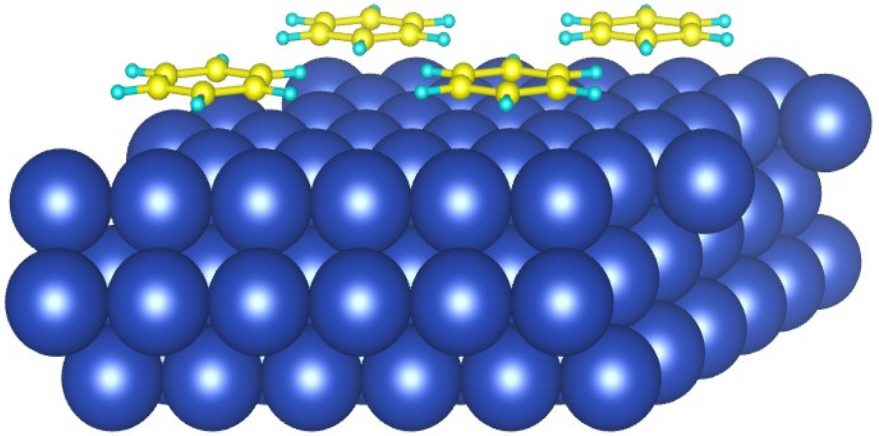
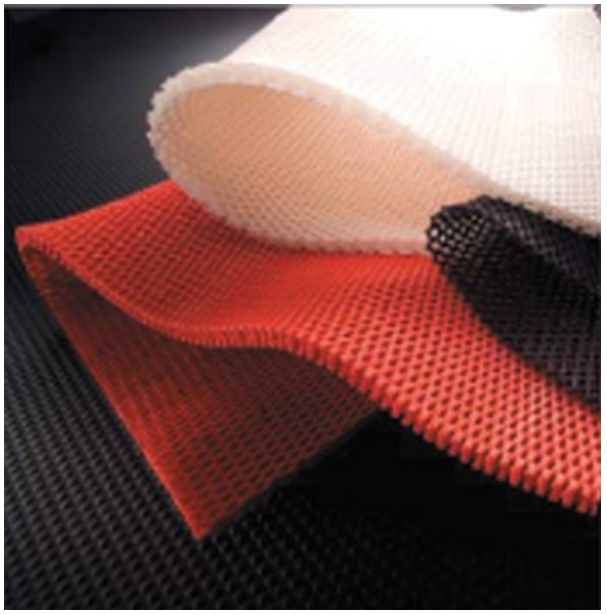
van der Waals (vdW) Interactions in Physics, Chemistry, and Materials Science







Textbook picture of vdW interactions

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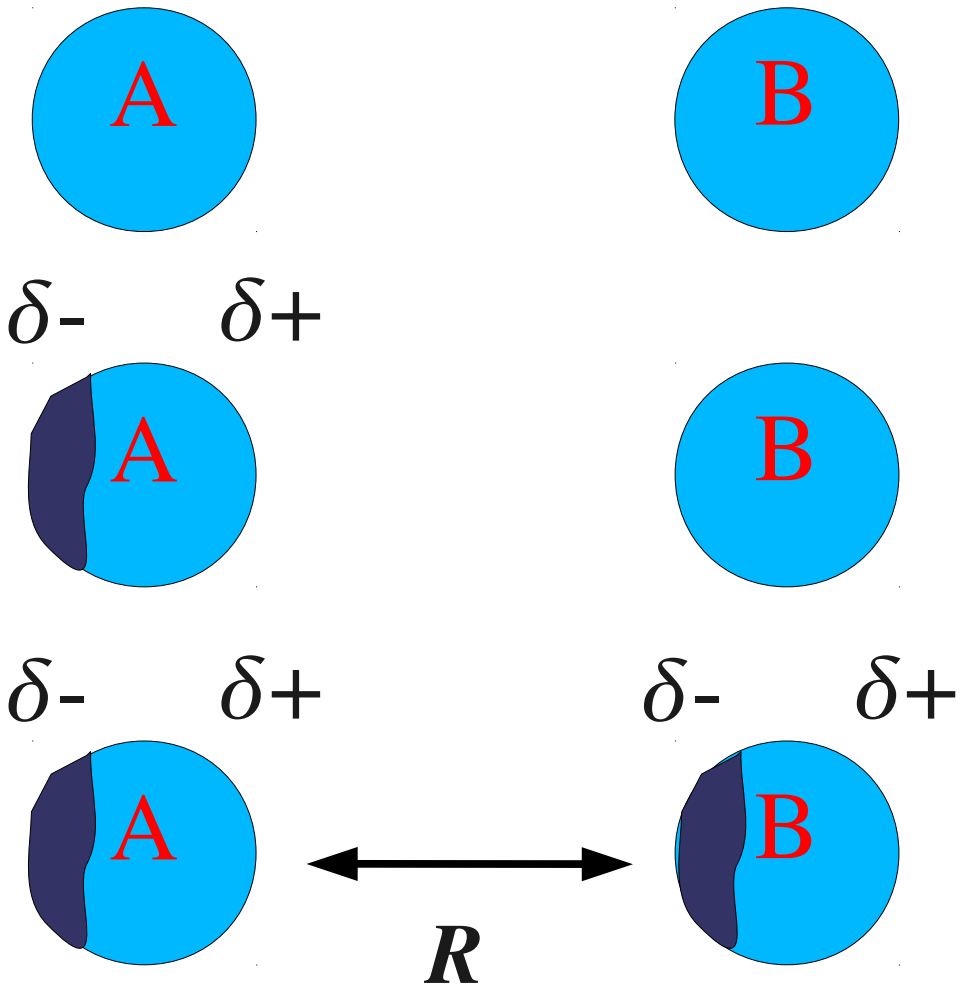
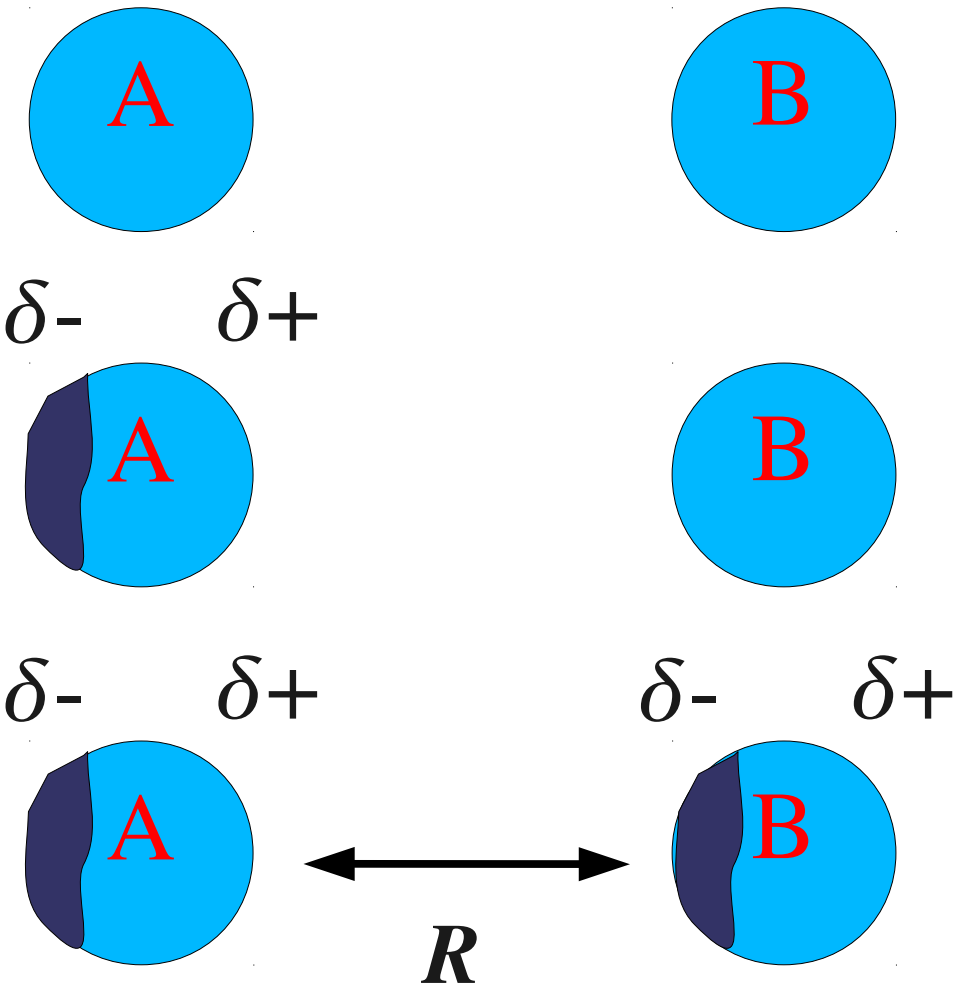
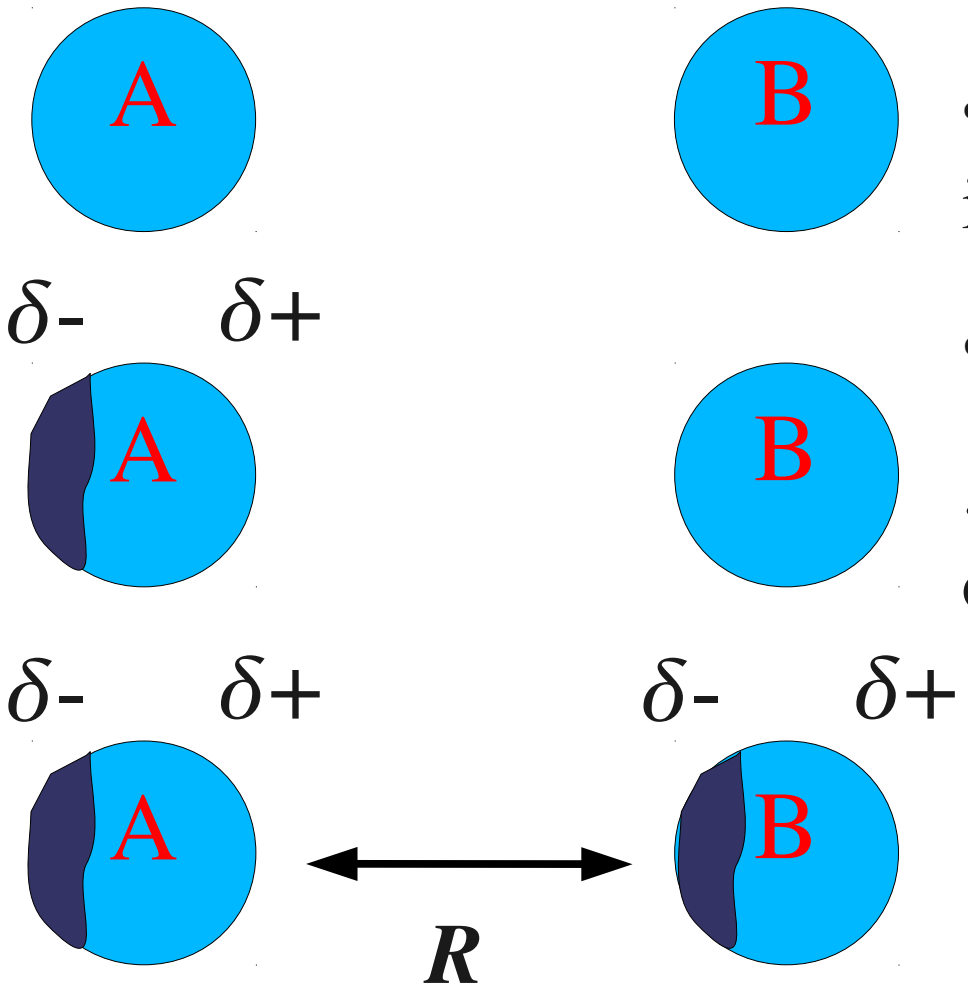


Textbook picture of vdW interactions



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

Textbook picture of vdW interactions



- **Ubiquitous** interatomic and intermolecular interaction
- Scales with system size

... **and** it is a significant component of *binding energies* in large systems!

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

Experimental "proof" for atom-atom vdW interaction

PRL **110,** 263201 (2013)

Selected for a Viewpoint in *Physics*
PHYSICAL REVIEW LETTERS

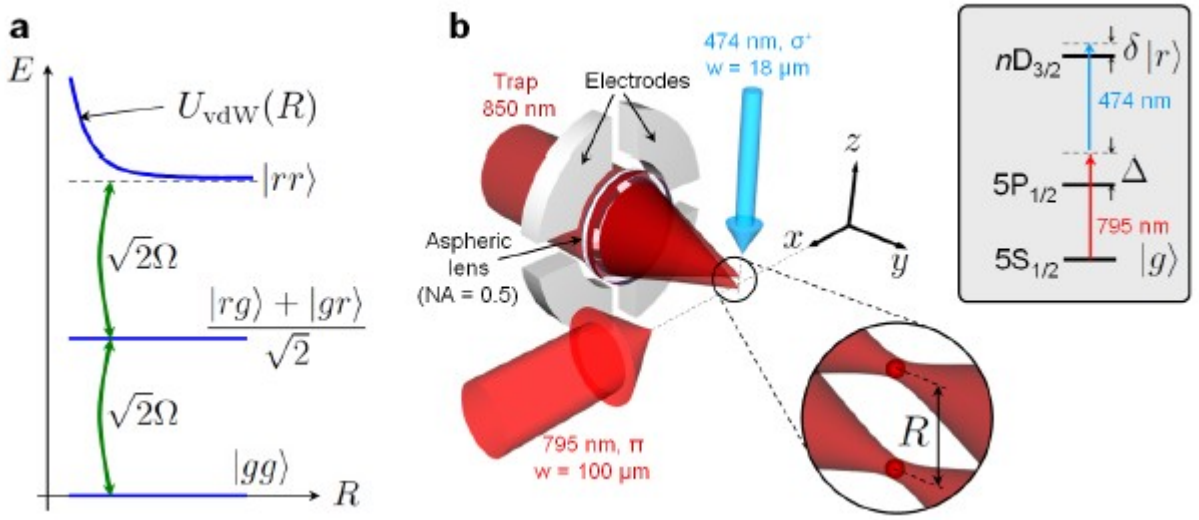
week ending
28 JUNE 2013

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

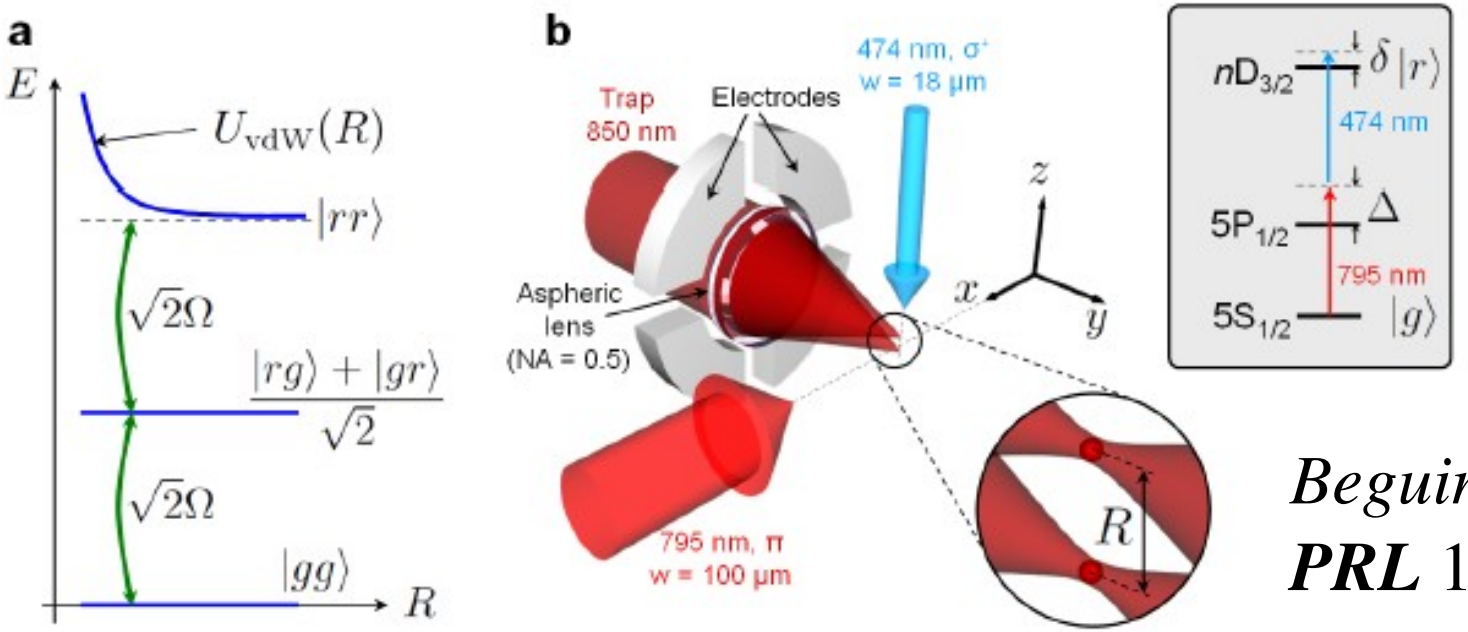
L. Béguin,[1] A. Vernier,[1] R. Chicireanu,[2] T. Lahaye,[1] and A. Browaeys[1]

[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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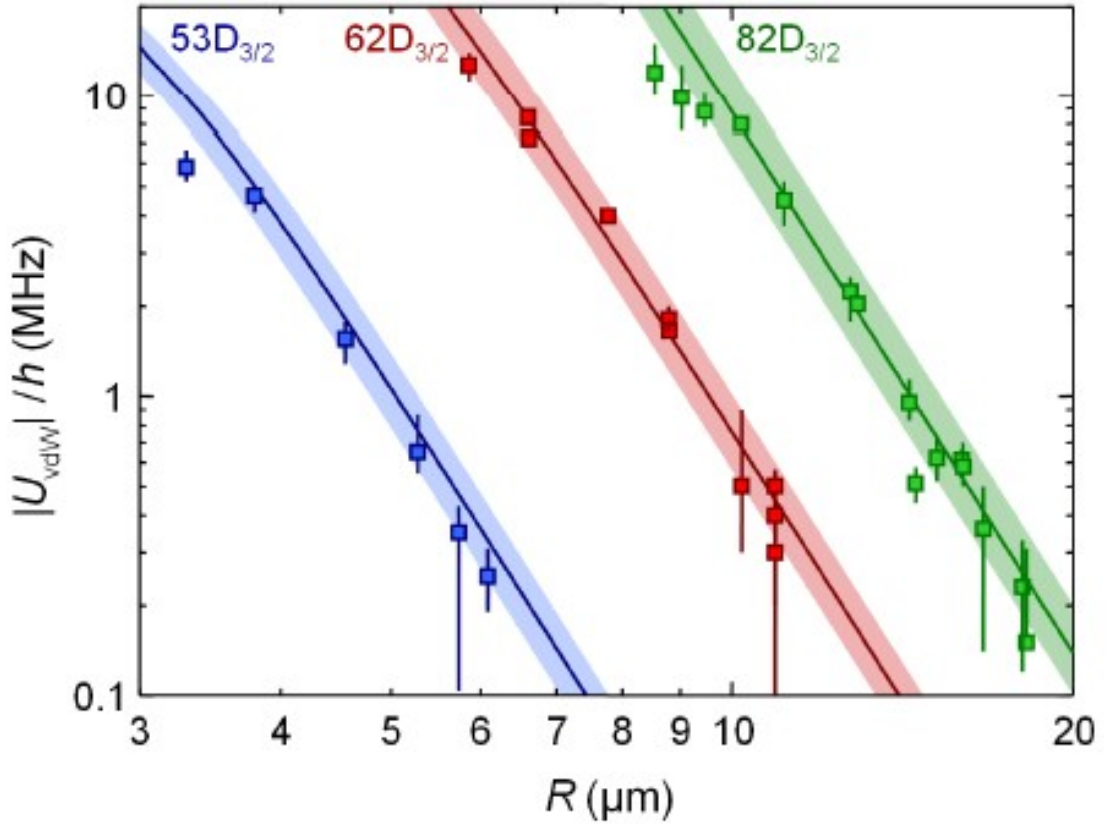
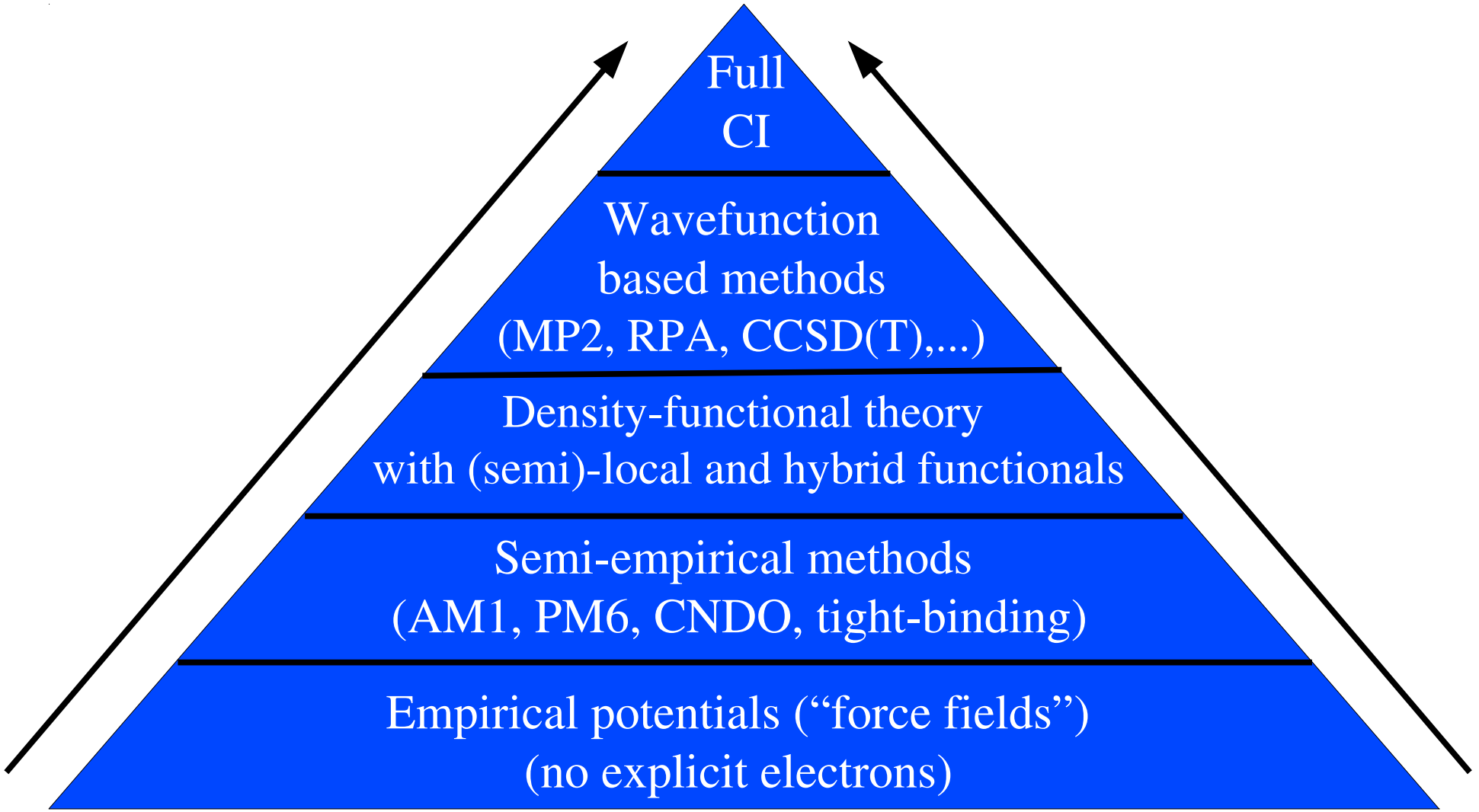


Current state-of-the-art of atomistic modeling

$$\hat{\mathcal{H}}\Psi = E\Psi$$



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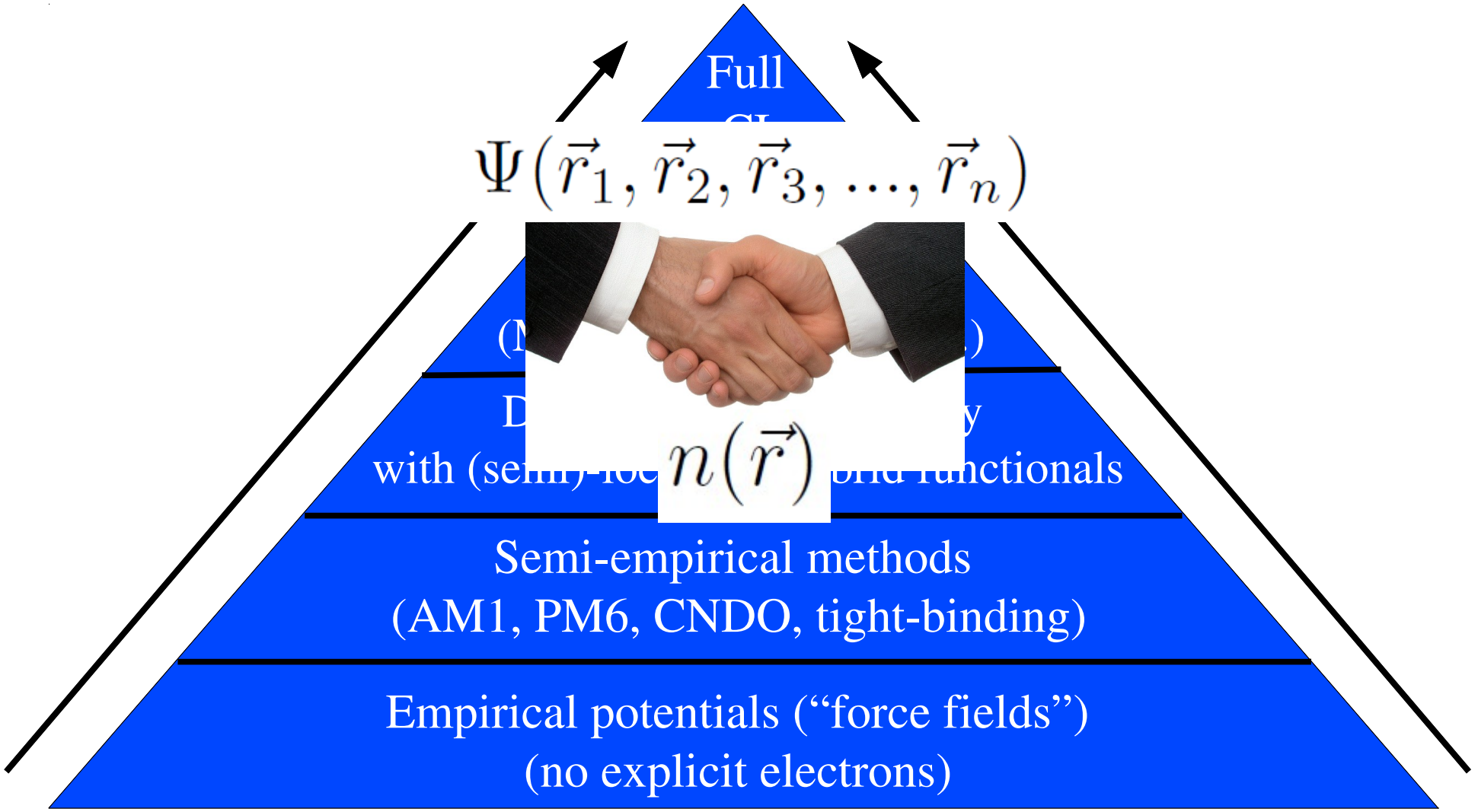
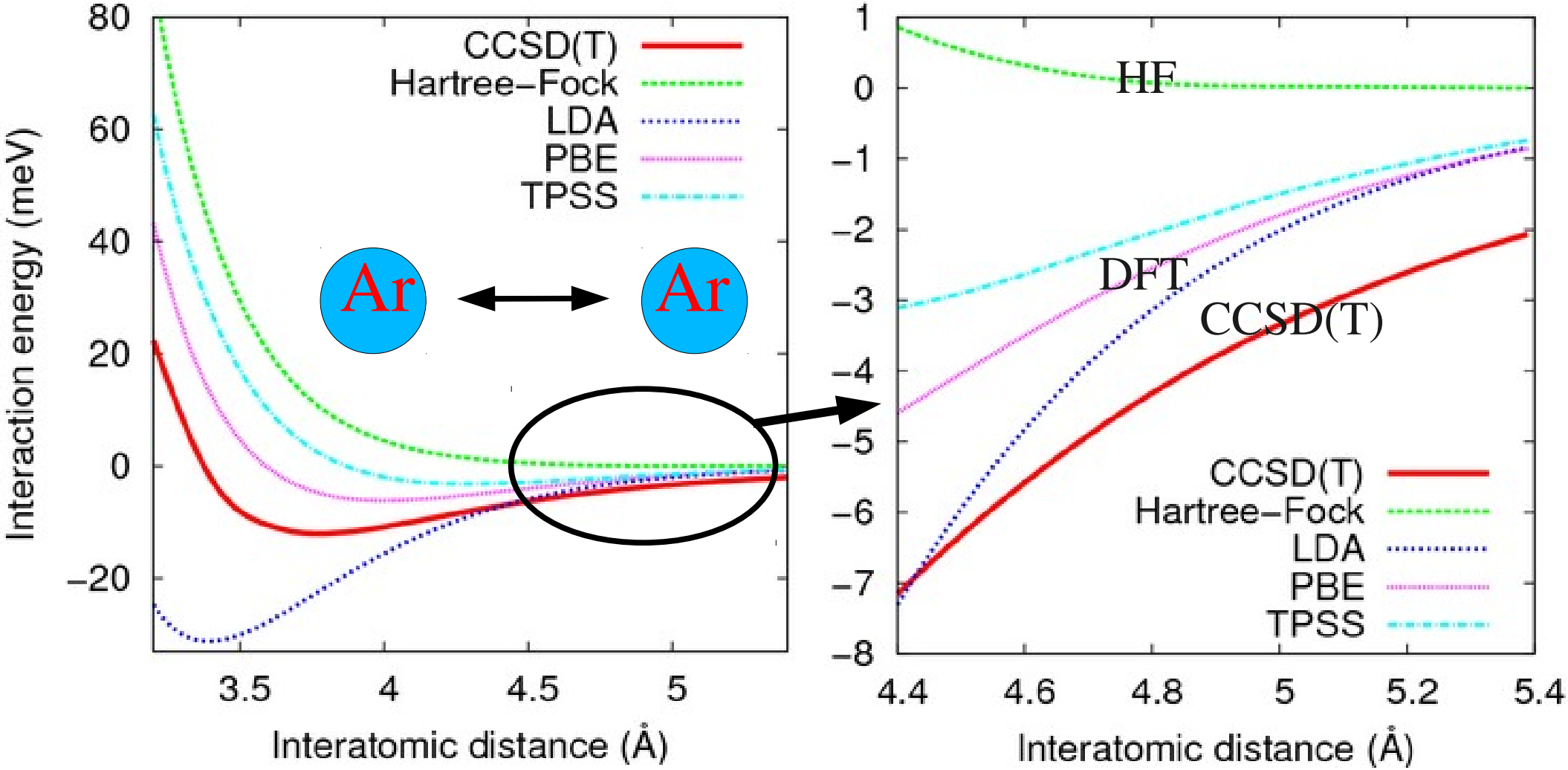


Failure of DFT approximations for (long-range) van der Waals interactions

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



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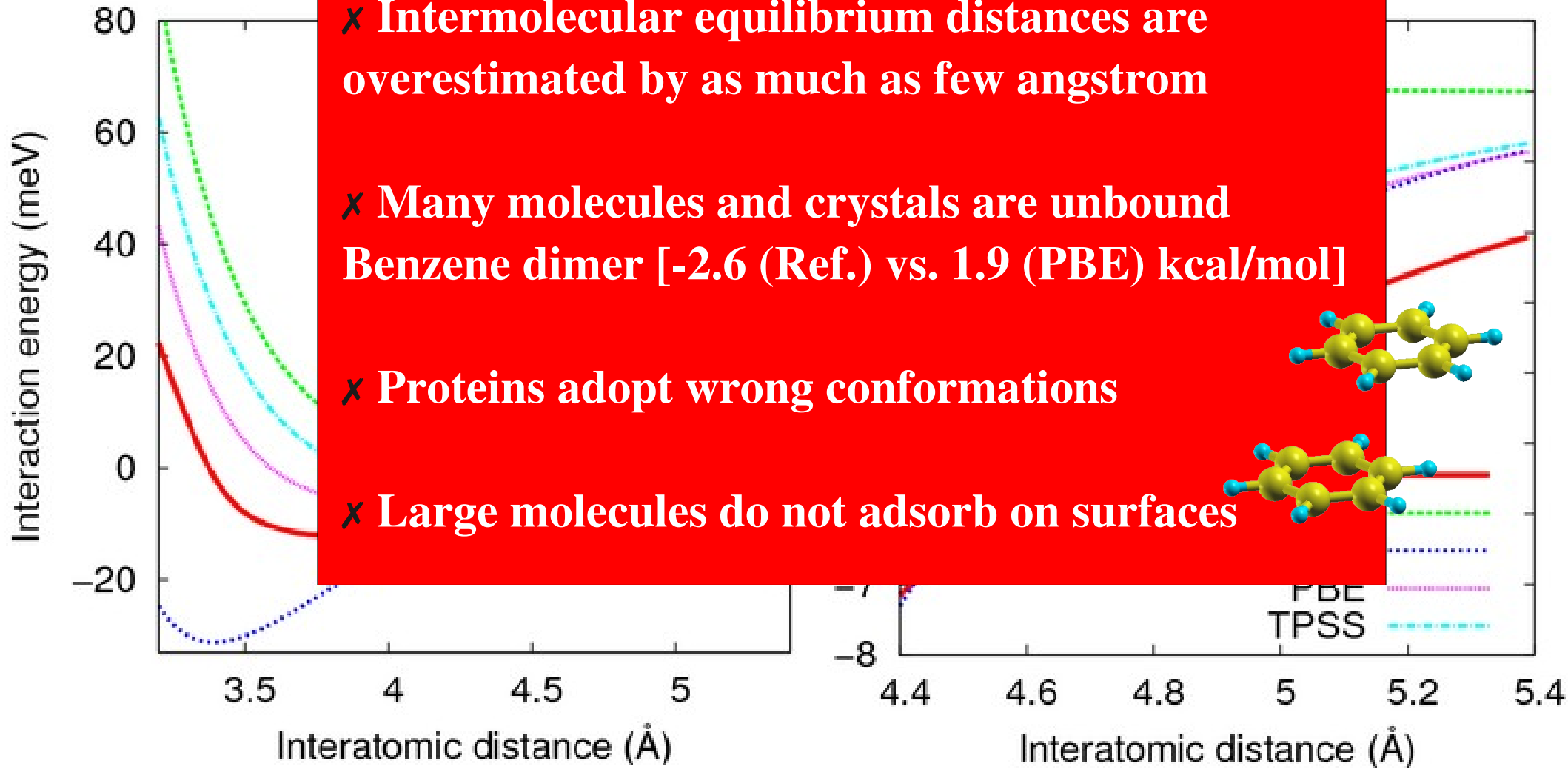
- ✗ Intermolecular equilibrium distances are overestimated by as much as few angstrom
- ✗ Many molecules and crystals are unbound
  Benzene dimer [-2.6 (Ref.) vs. 1.9 (PBE) kcal/mol]
- ✗ Proteins adopt wrong conformations
- ✗ Large molecules do not adsorb on surfaces



(Approximate)
vdW-inclusive DFT methods

Review:

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

Concepts and methods for dispersion in DFT

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

Concepts and methods for dispersion in DFT

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

- Non-local functionals (depend explicitly on ***r*** and ***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

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

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

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

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

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

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

vdW-DF-04

- Exchange: revPBE
- Local corr.: LDA
- No free parameters
- C_6 error: ~ 20%

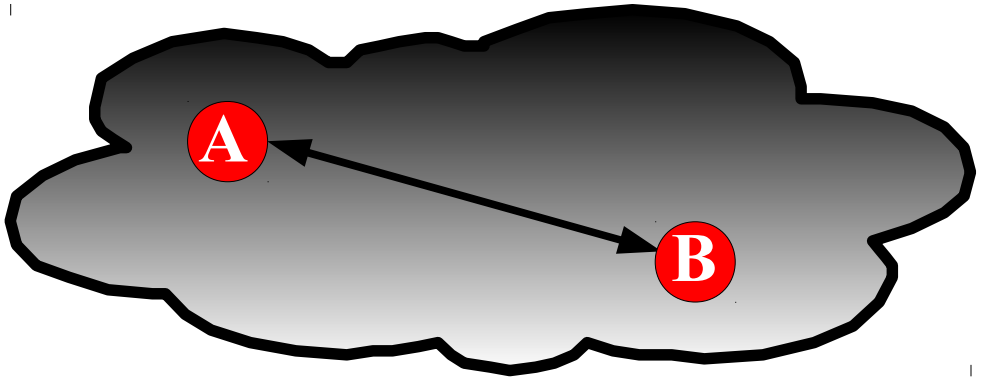
vdW-DF-10

- Exchange: PW86
- Local corr.: LDA
- 2 parameters
- C_6 error: ~ 40%(*)

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

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

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



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

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

Interatomic methods for vdW interactions

Interatomic vdW methods

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

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

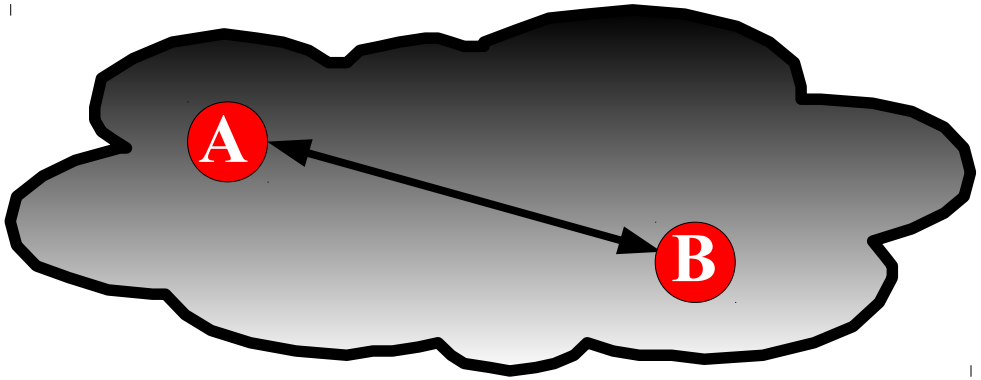
- Two parameters per atomic pair: (1) VdW C_6 interaction coefficient and (2) vdW radius.
- Clearly, if (1) and (2) are empirical, this leads to many fitting parameters. This was frequently the case before 2008.

Evolution of interatomic vdW methods

- Grimme's D1,D2,D3 (2004,2006,2010): 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 ~ 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 ?

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

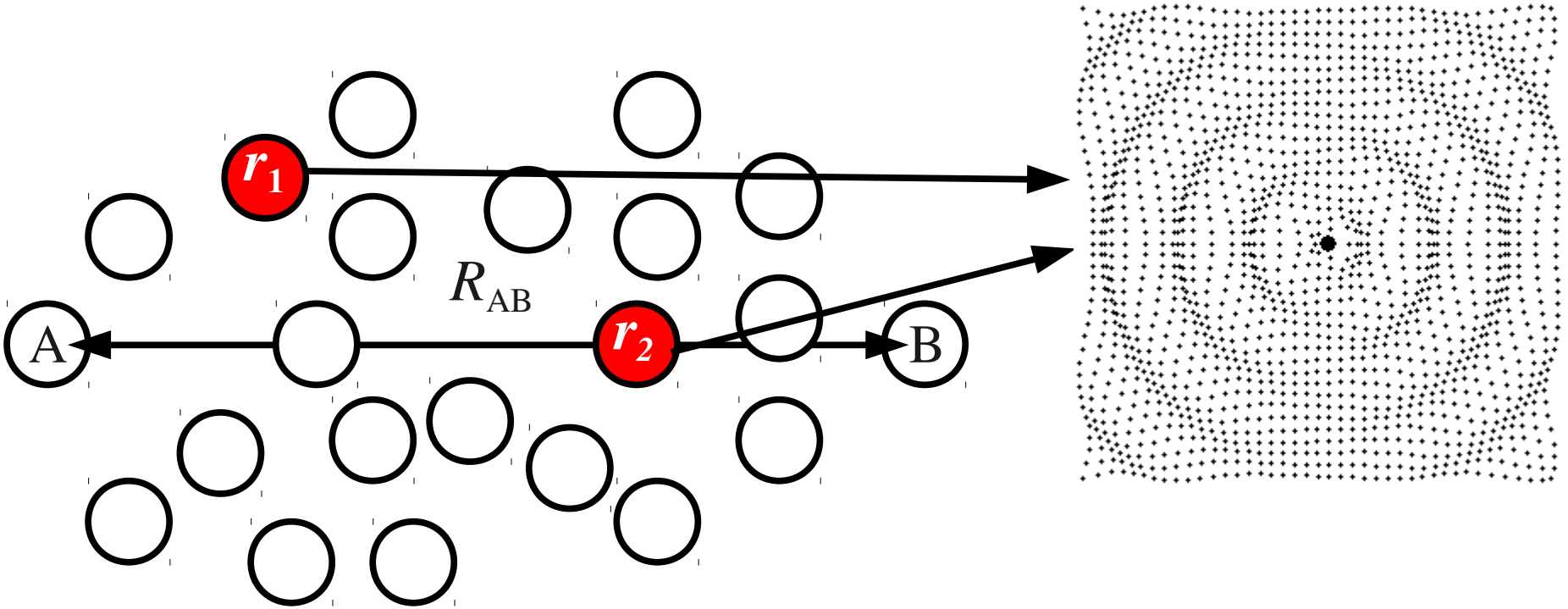


1) Long-range electrodynamic response for fluctuating dipoles
2) Non-additive many-body vdW energy beyond two-body

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

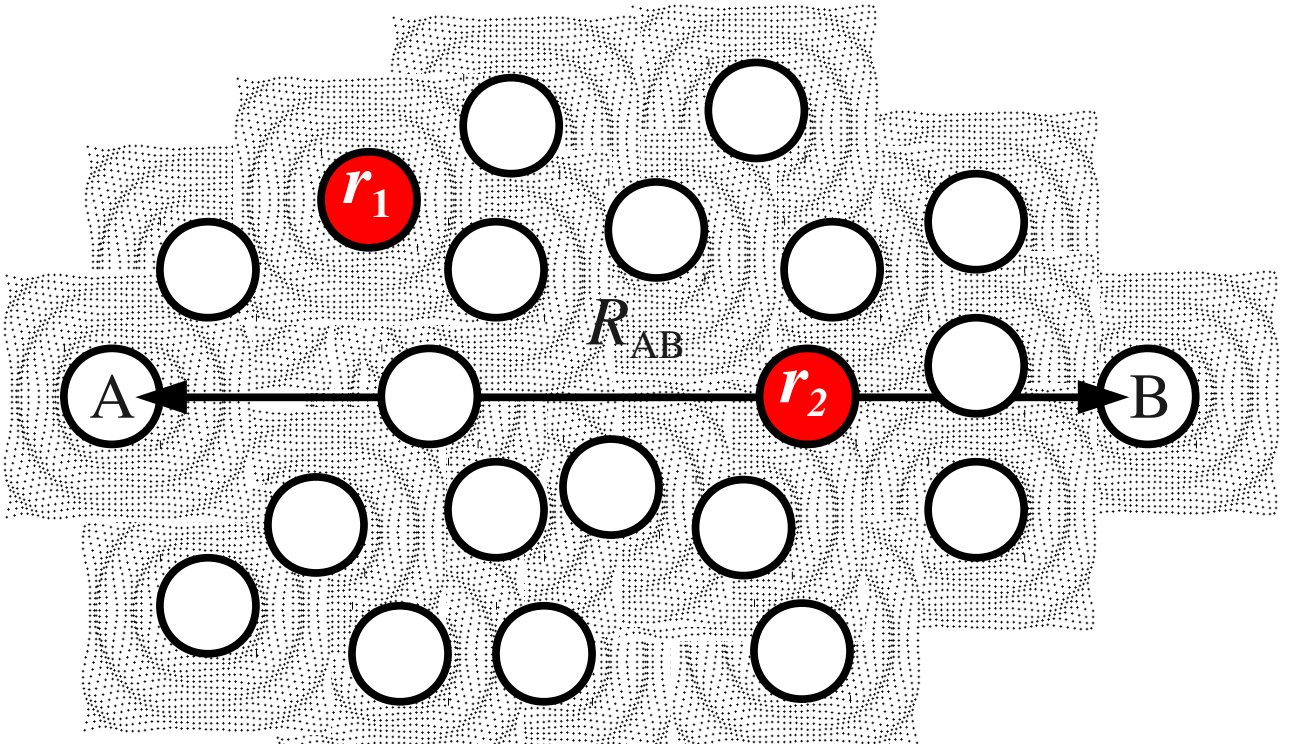
Beyond textbook picture of vdW interactions

Beyond textbook model of vdW interactions: Electrodynamic response effects



Many-body electrodynamic response effects:
From electron density to response functions

$$\chi_\lambda(\vec{r}_1, \vec{r}_2; \omega) \quad 0 \leq \lambda \leq 1$$



$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \longmapsto \frac{\lambda}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Many-body electrodynamic response effects:
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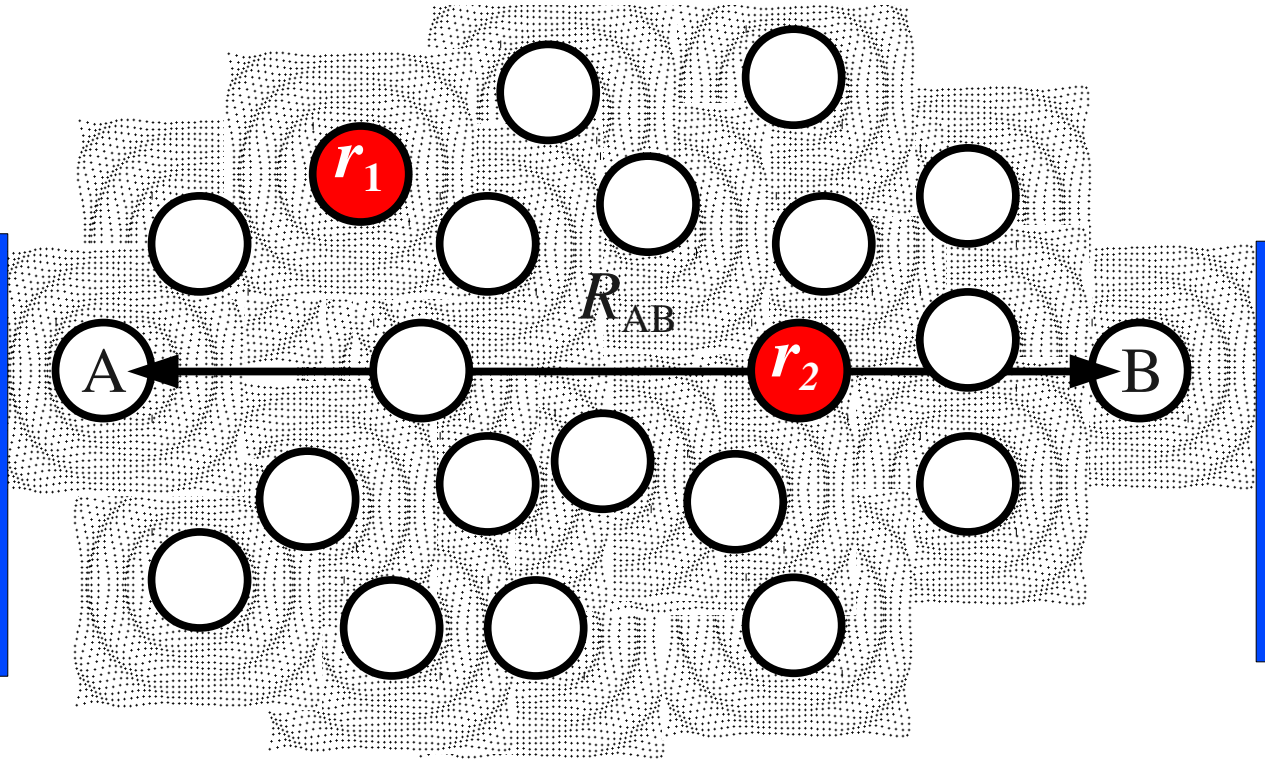
$$\chi_\lambda(\vec{r}_1, \vec{r}_2; \omega) \quad 0 \leq \lambda \leq 1$$

1

Accurate Microscopic Modeling of Coulomb Response



2

Full (All-Order) Many-Body Correlation Energy (includes vdW)

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \longmapsto \frac{\lambda}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Many-body electrodynamic response effects:
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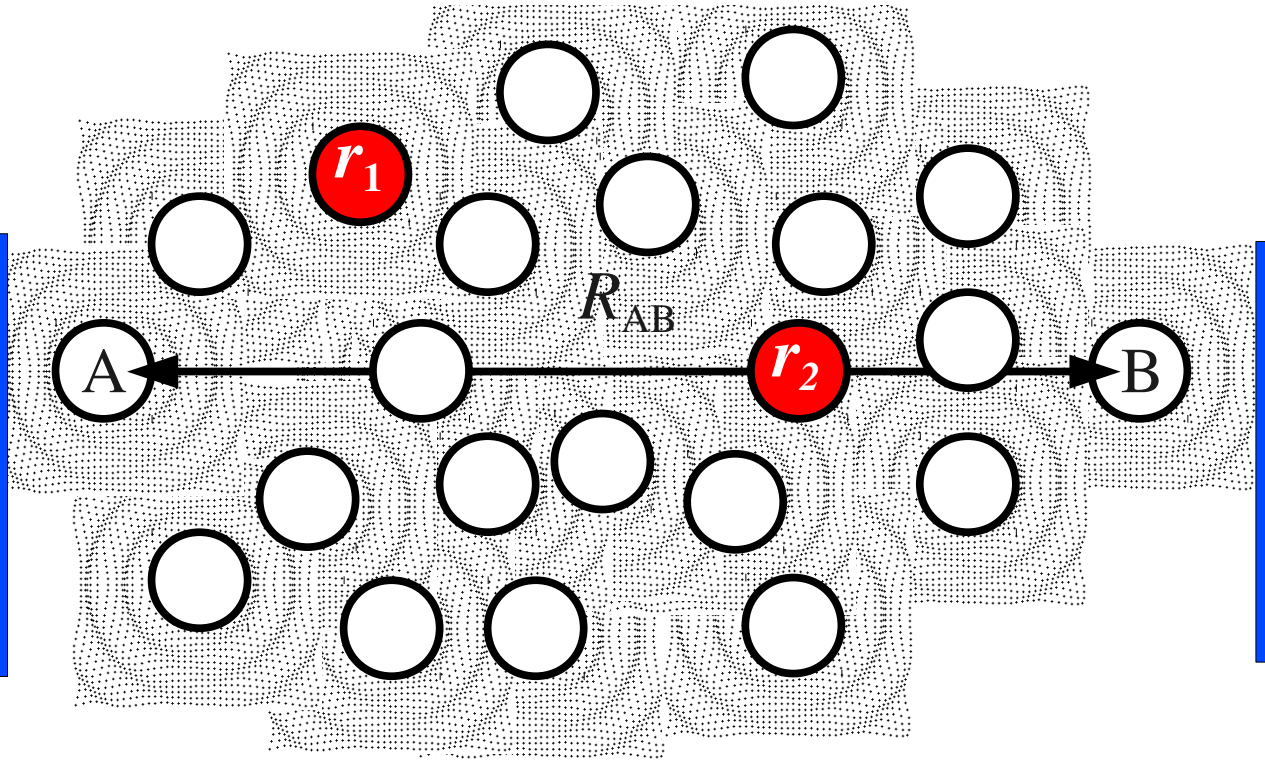


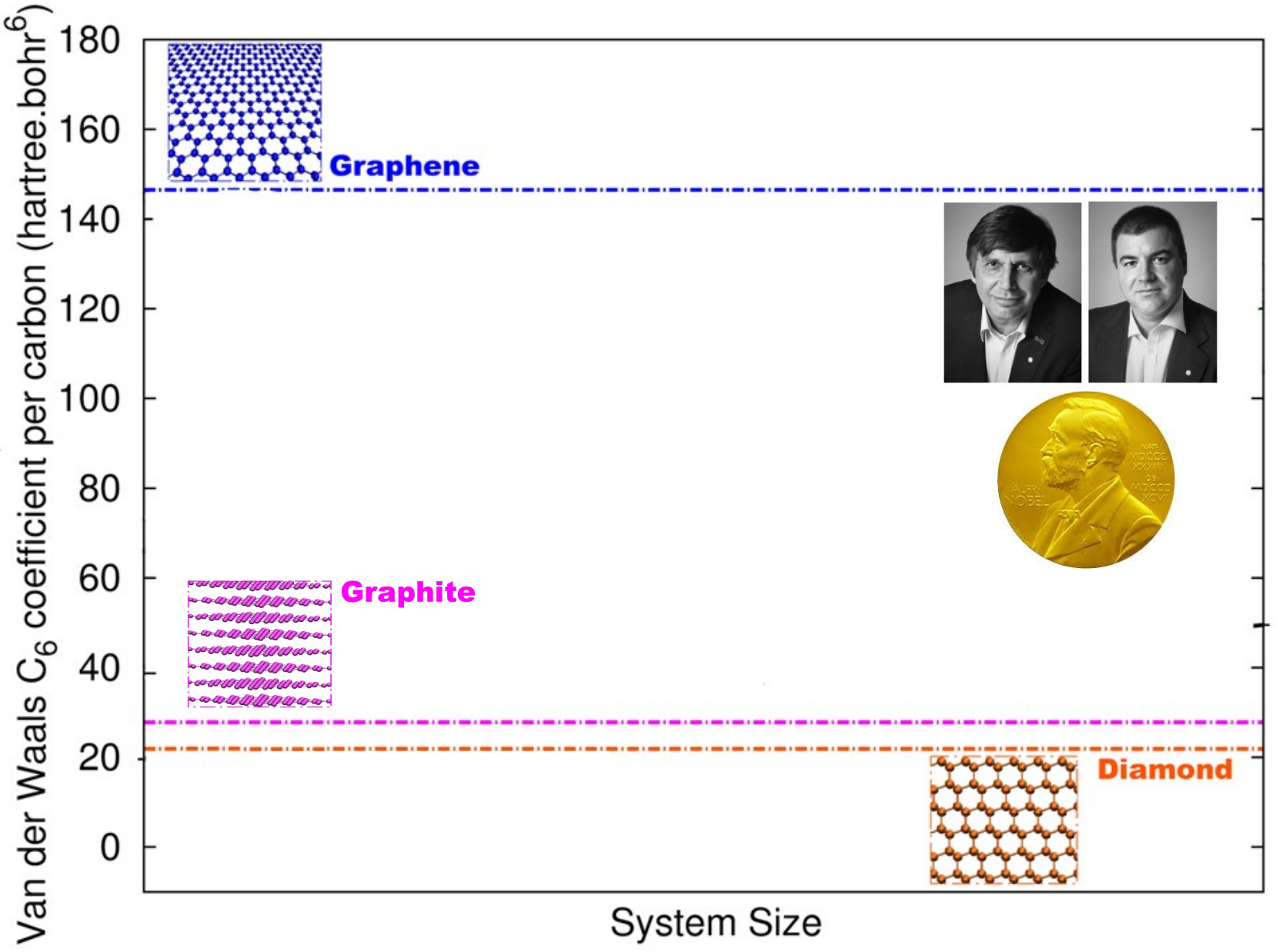
2

Full (All-Order) Many-Body Correlation Energy (includes vdW)

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

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

Electrodynamic treatment of vdW interactions: beyond "hybridized atoms"



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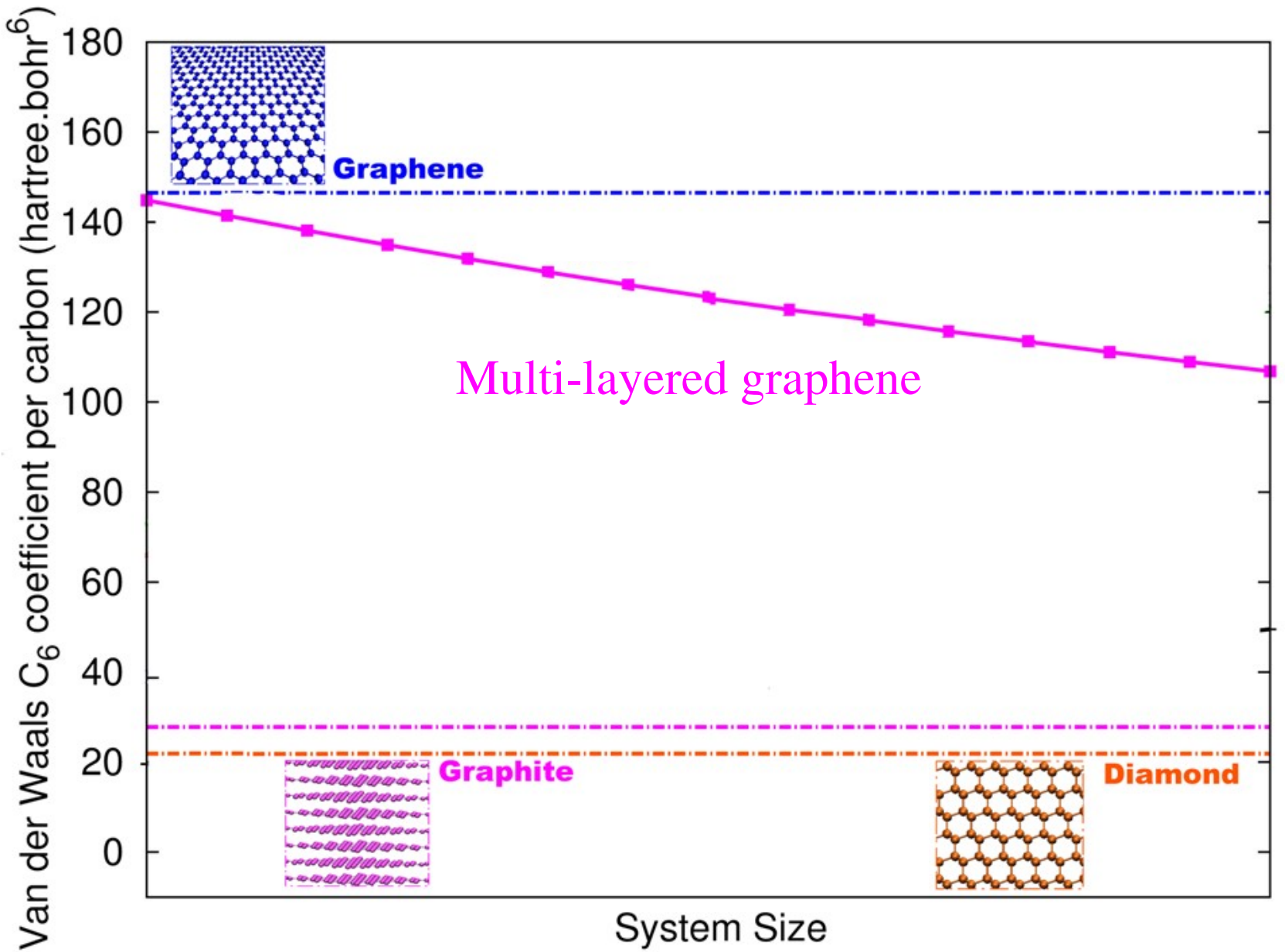

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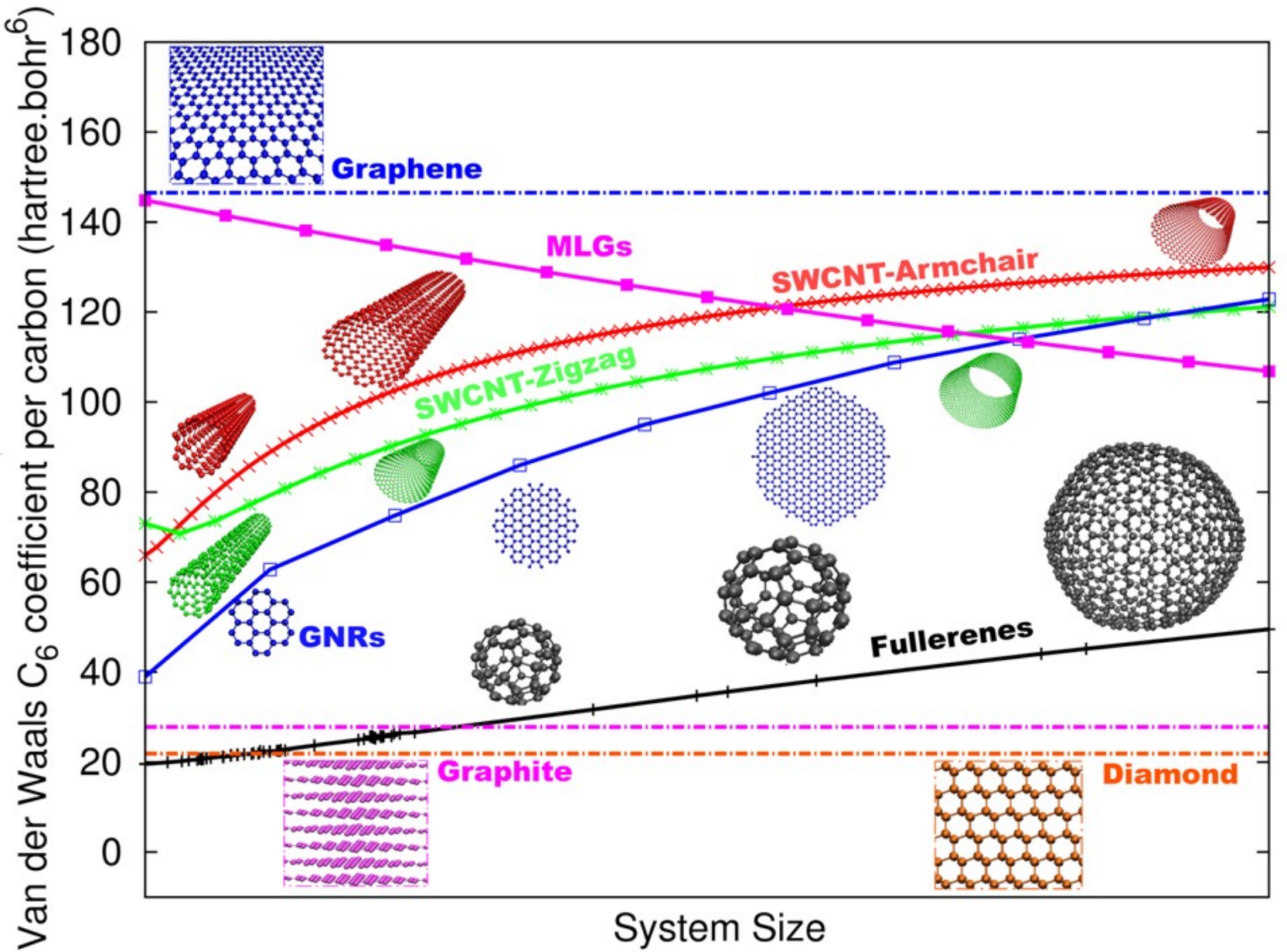

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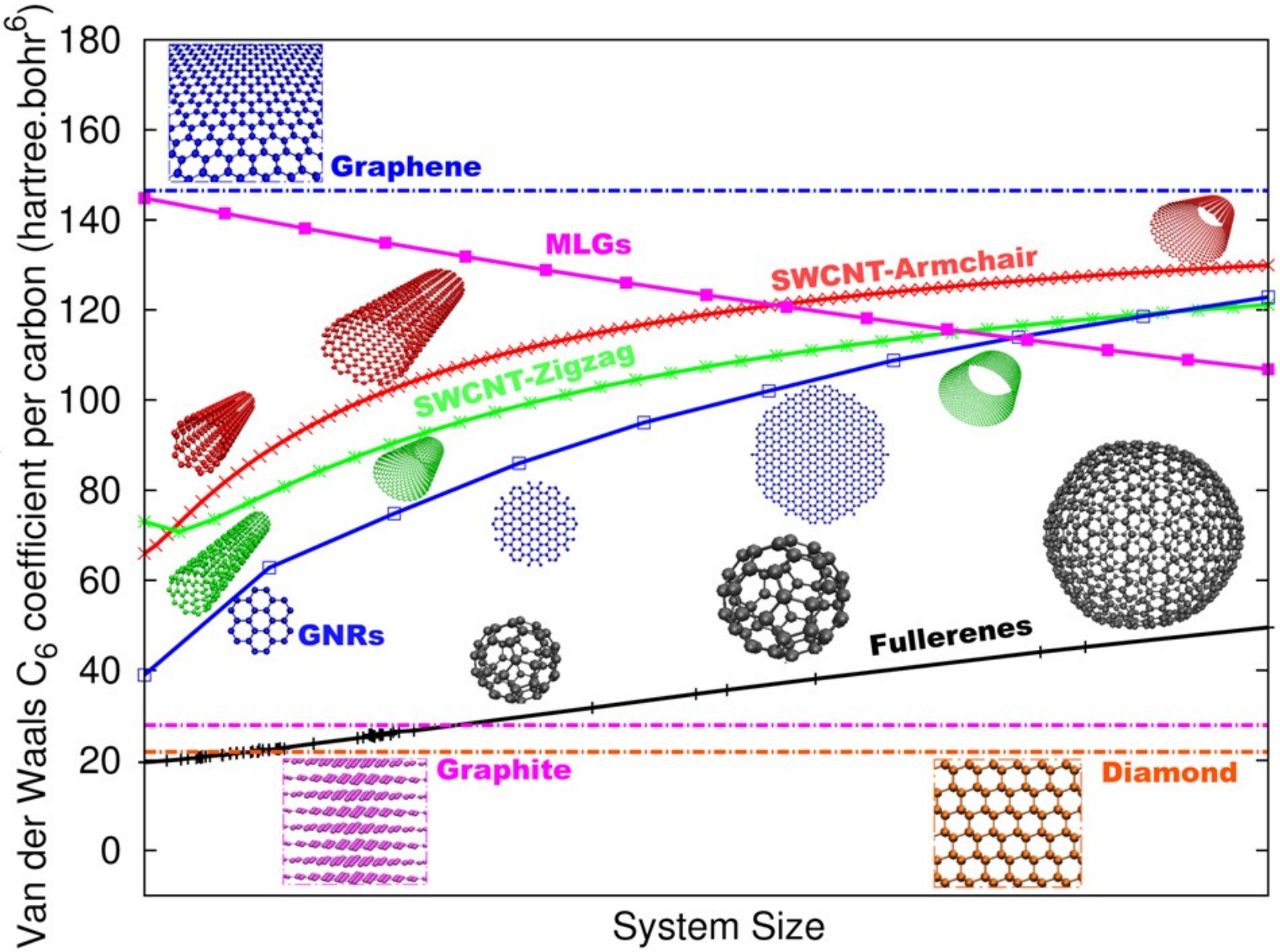

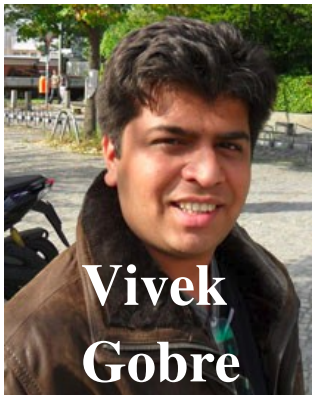

V. V. Gobre and A. Tkatchenko, ***Nature Comm.*** (2013)

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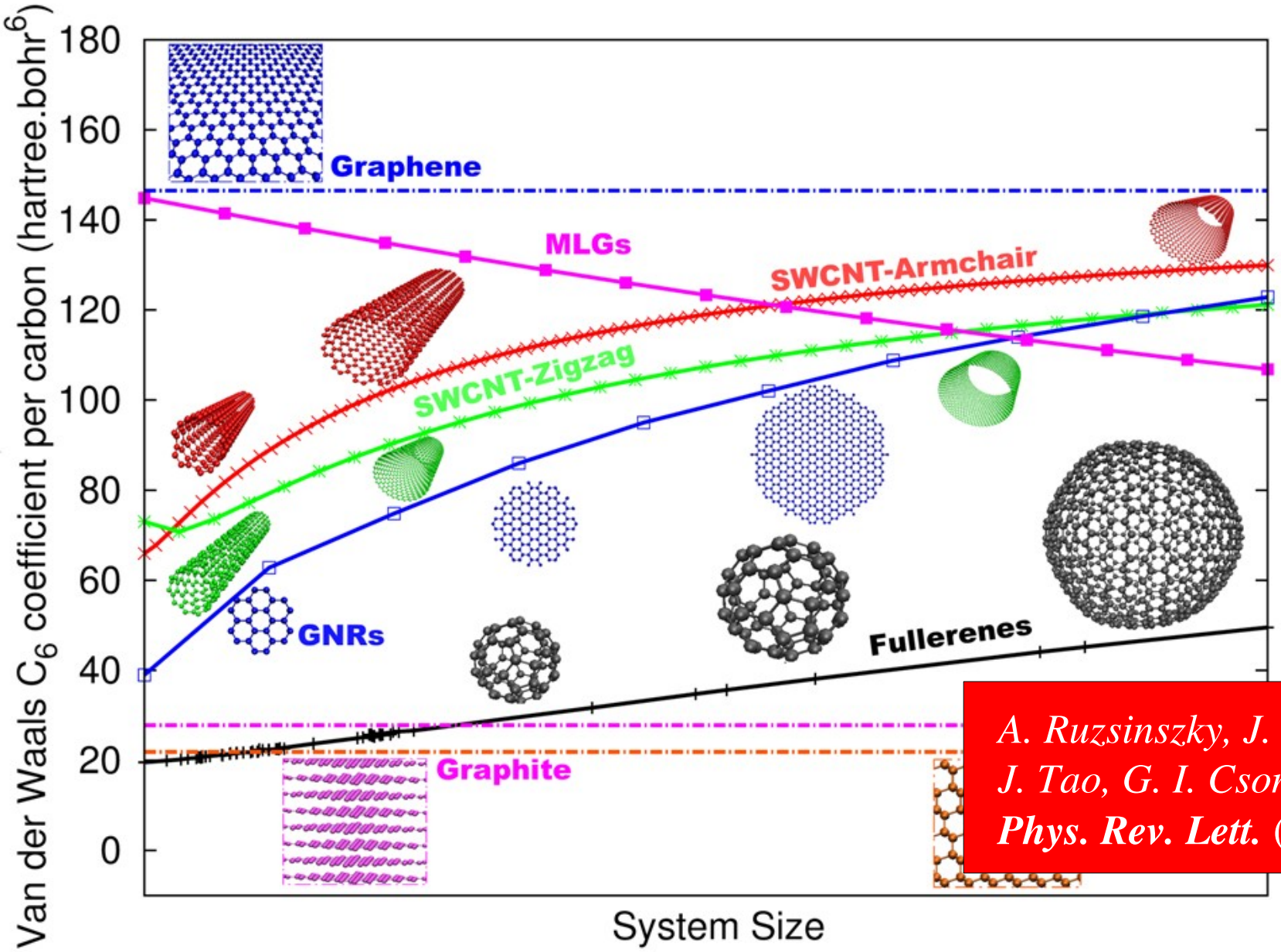
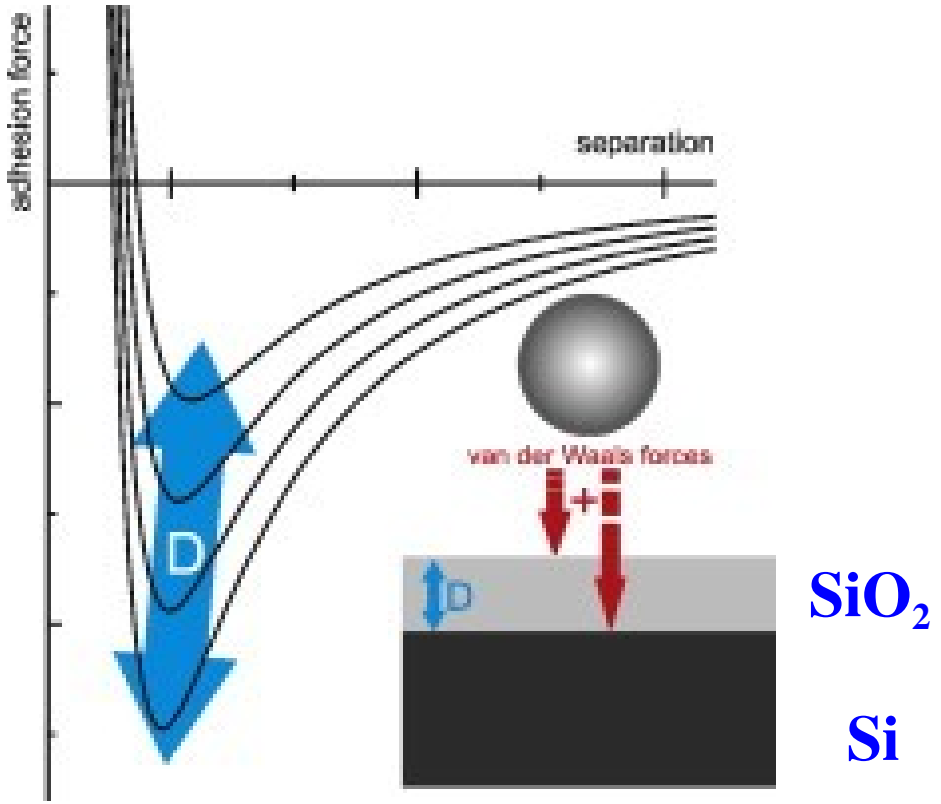


A. Ruzsinszky, J. P. Perdew, J. Tao, G. I. Csonka, J. M. Pitarke, ***Phys. Rev. Lett.*** (2012).

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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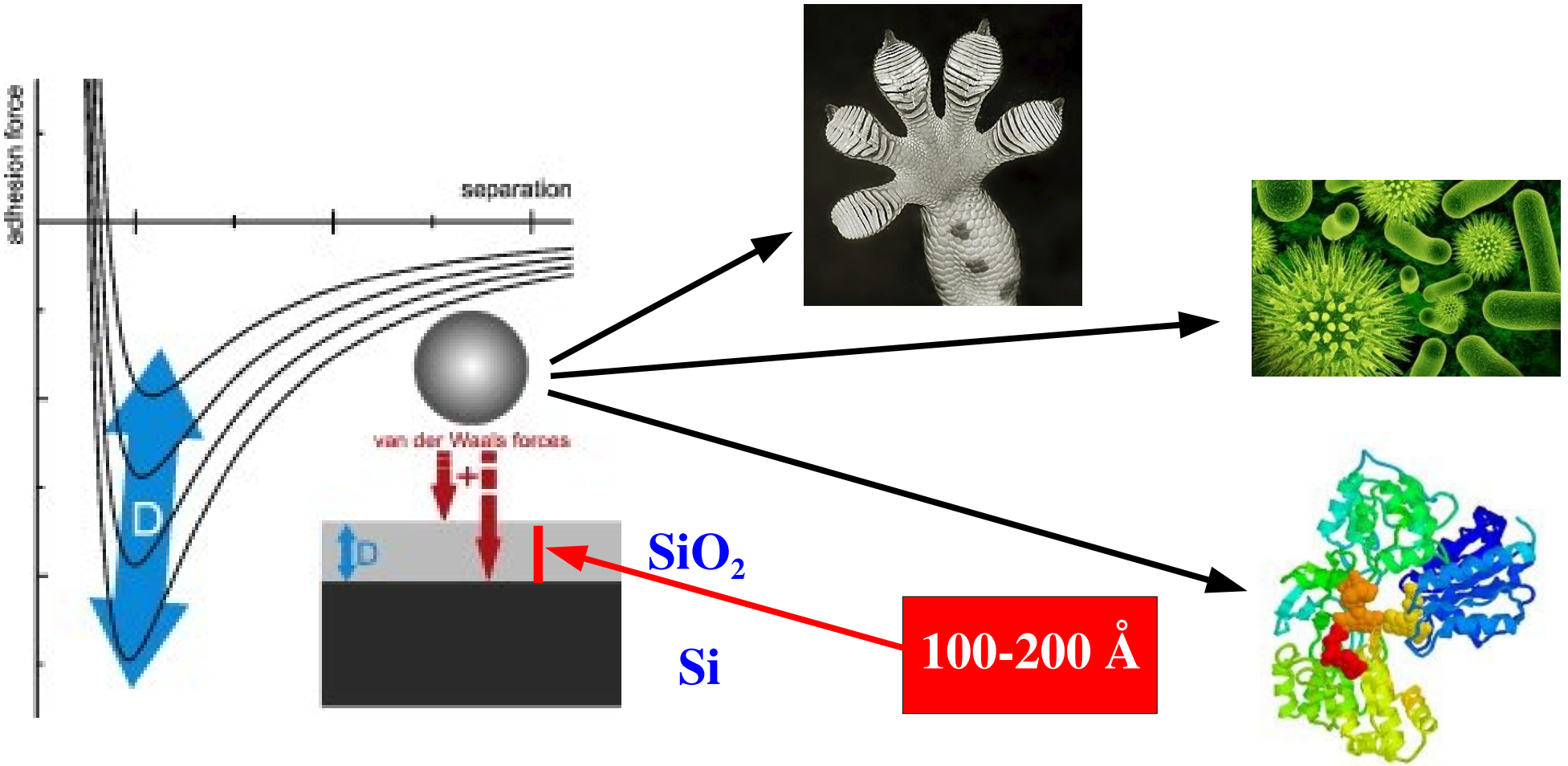

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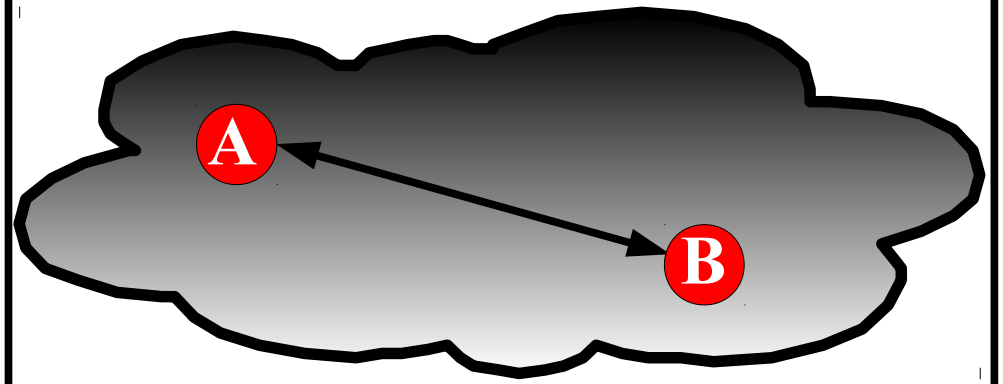
P. Loskill, J. Puthoff, M. Wilkinson, K. Mecke, K. Jacobs and K. Autumn, ***J. R. Soc. Interface,*** *to be published* (2013).

Towards Efficient Many-Body Treatment of van der Waals Correlations

The conventional approach

(Grimme/2004, Johnson-Becke/2008, Tkatchenko-Scheffler/2009, Langreth-Lundqvist/2004,2010, Vydrov-van Voorhis/2011, ...)

Effective screening and two-body energy



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

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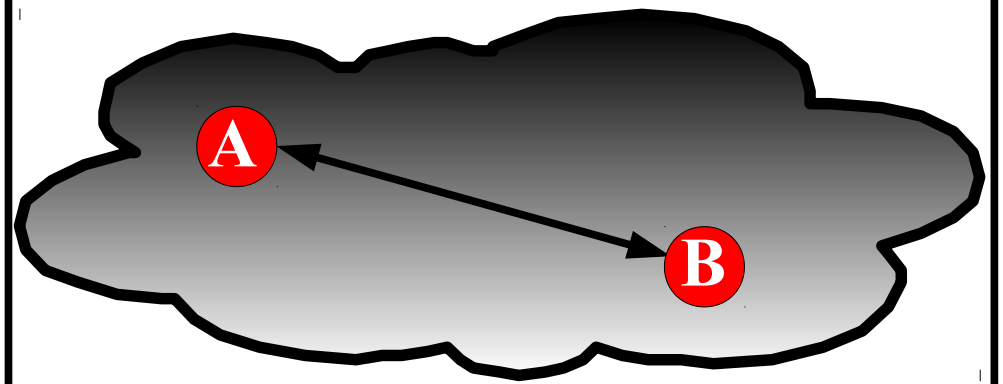
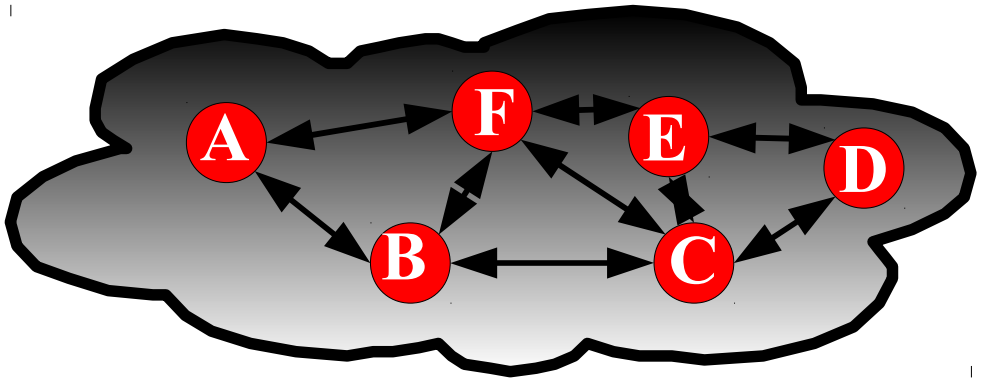


Valid for small molecules ***or*** homogeneous dielectrics

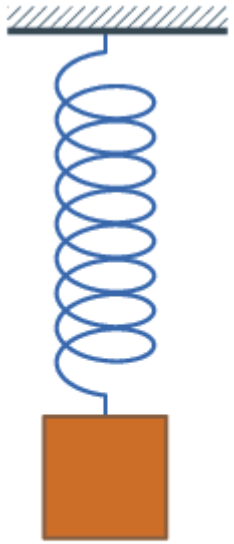
The new state-of-the-art

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



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

The Model:
Quantum Harmonic Oscillator (QHO)



Nucleus (q)

Harmonic bond (ω)

"Electron" ($-q$,m)

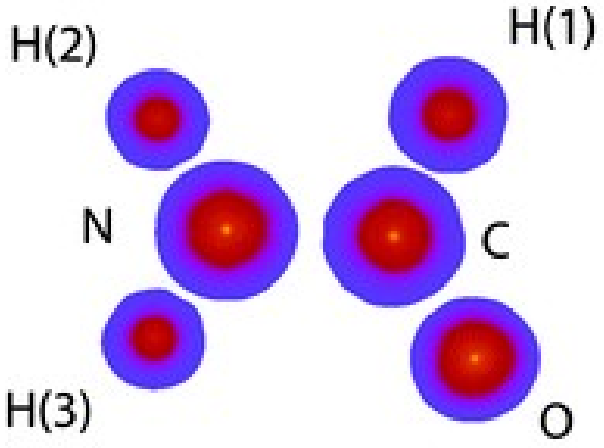
In the dipole approximation:

(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.

Quantum Harmonic Oscillators in Molecules and Solids from First Principles

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



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

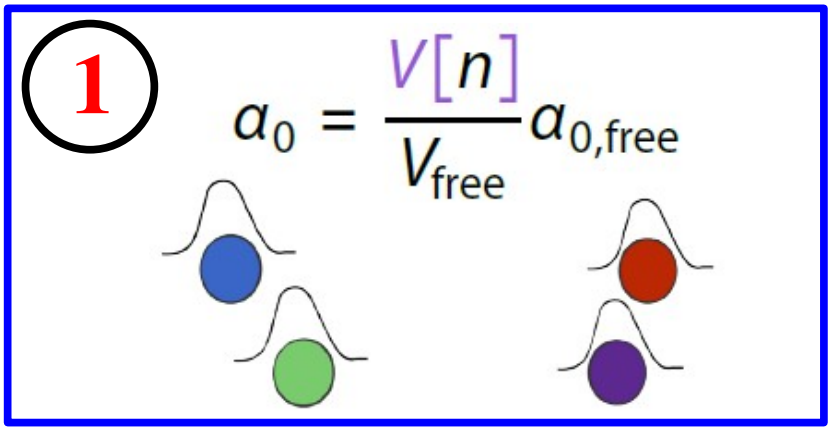
$\boldsymbol{\alpha}^0$ and $\boldsymbol{\omega}^0$ include short-range hybridization

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

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

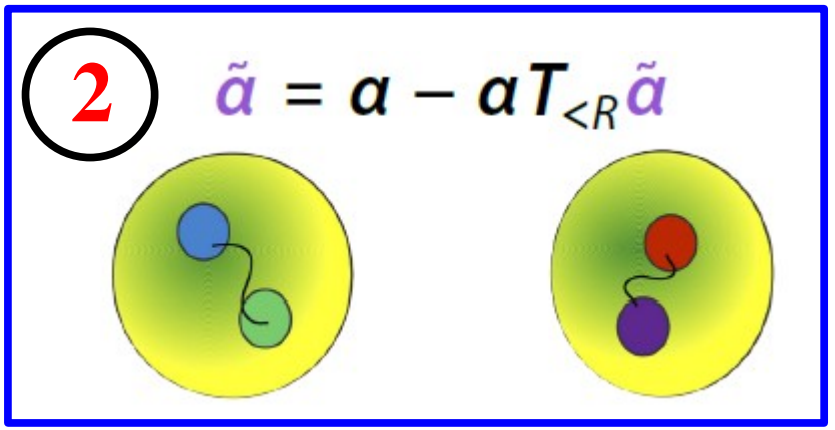
DFT+Many-Body-Dispersion (MBD) method

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



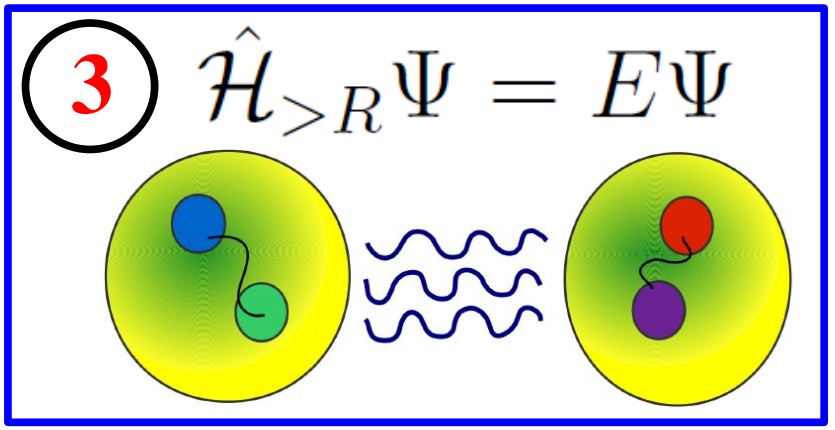
Valence electrons projected to oscillators

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



Dyson-like short-range electrodynamic screening

A. Ambrosetti, R. A. Distasio Jr., A. M. Reilly, A. Tkatchenko, ***J. Chem. Phys.*** (2014)

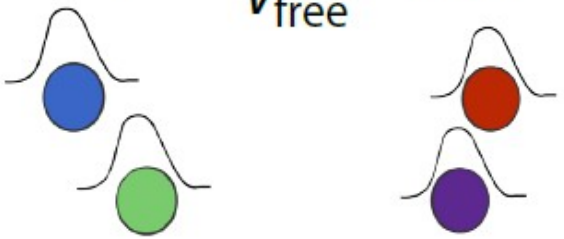


Long-range correlation energy calculated using ACFD

DFT+MBD method in a nutshell

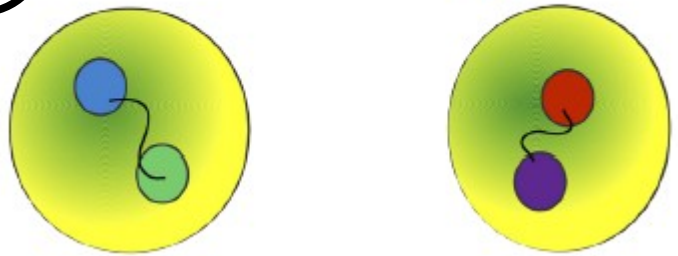
1

$$\alpha_0 = \frac{V[n]}{V_{\text{free}}} \alpha_{0,\text{free}}$$



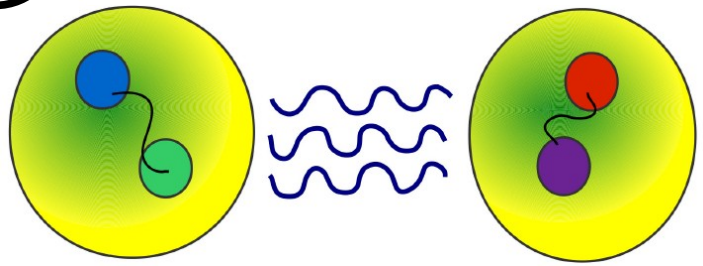
2

$$\tilde{\alpha} = \alpha - \alpha T_{<R} \tilde{\alpha}$$



3

$$\hat{\mathcal{H}}_{>R} \Psi = E \Psi$$

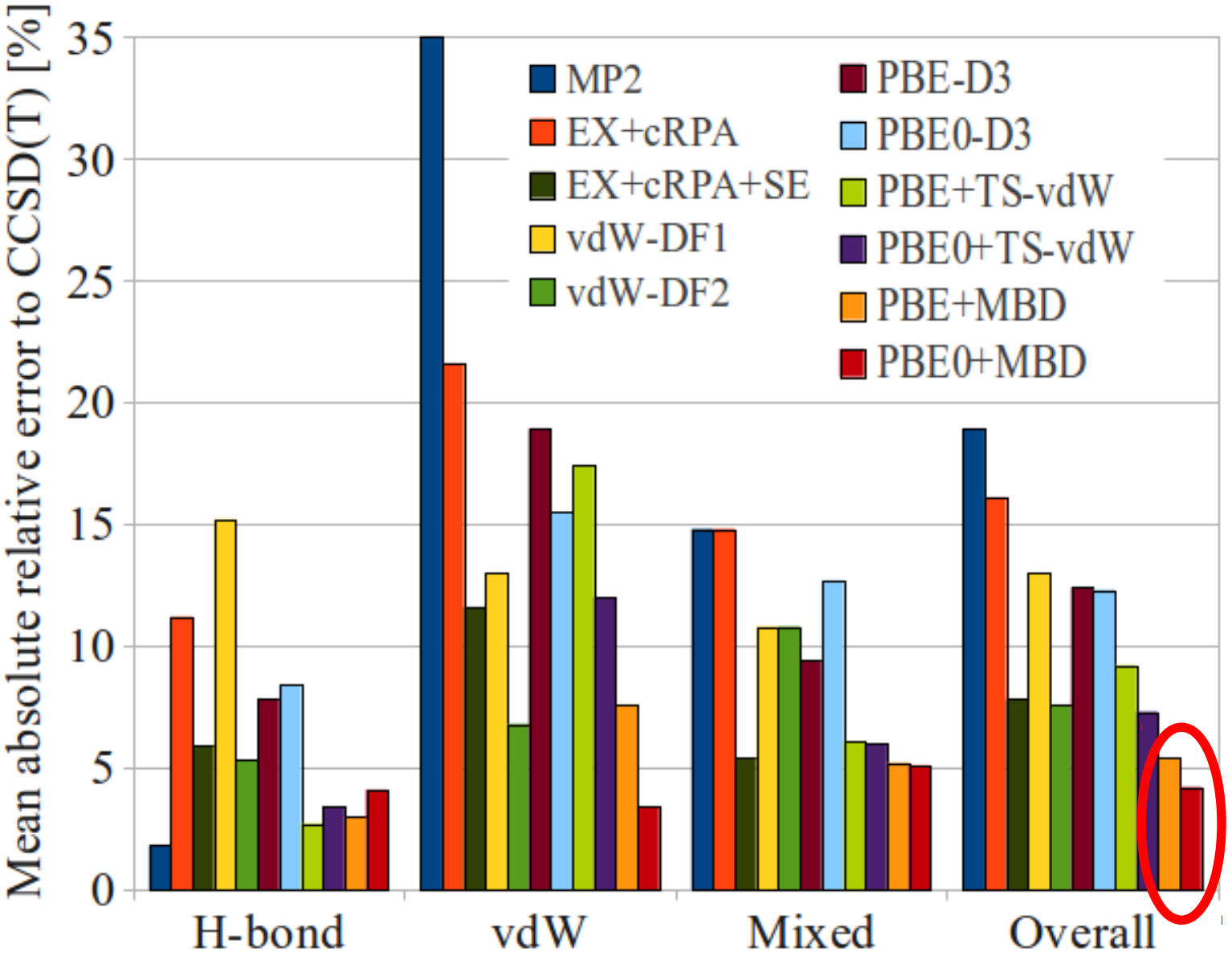


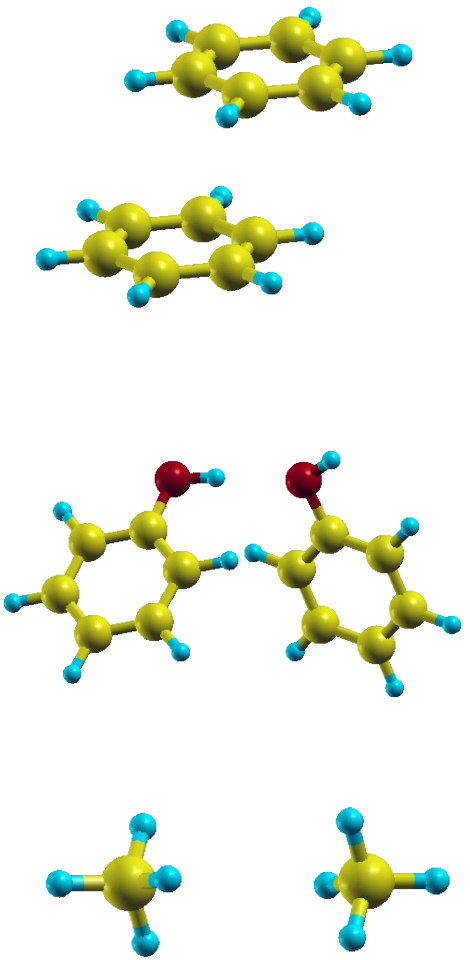
$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n)$$

$$n(\vec{r})$$

- Molecular and atom-in-a-solid polarizabilities and C_6 coefficients are accurate to 7%.
- Negligible cost compared to DFT (MBD calculations can be easily done for > 10,000 atoms, N^3 scaling).
- Single adjustable parameter to couple DFT and MBD.

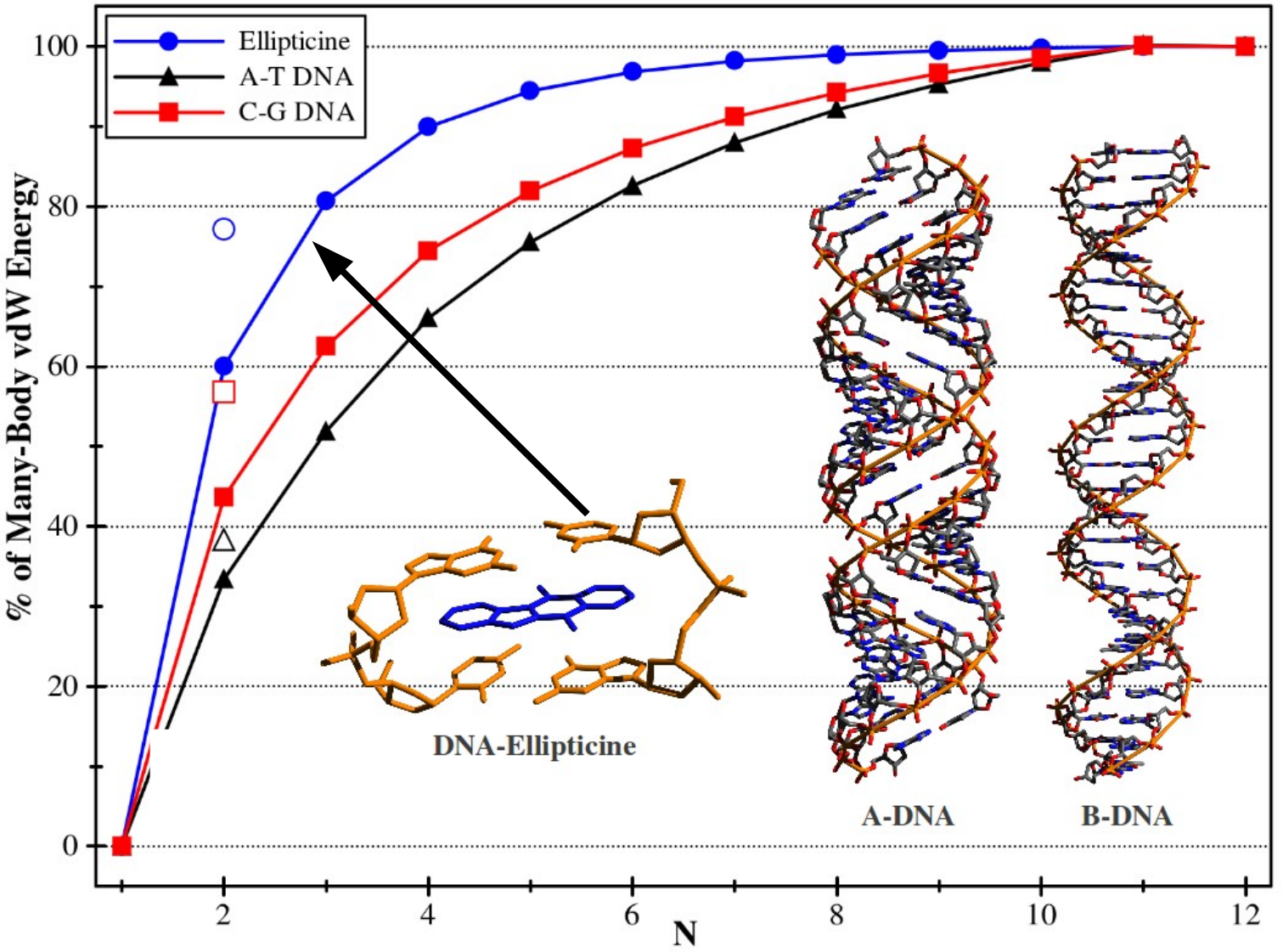
Performance of DFT+MBD for gas-phase intermolecular interactions





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

Large many-body vdW effects in complex molecular geometries

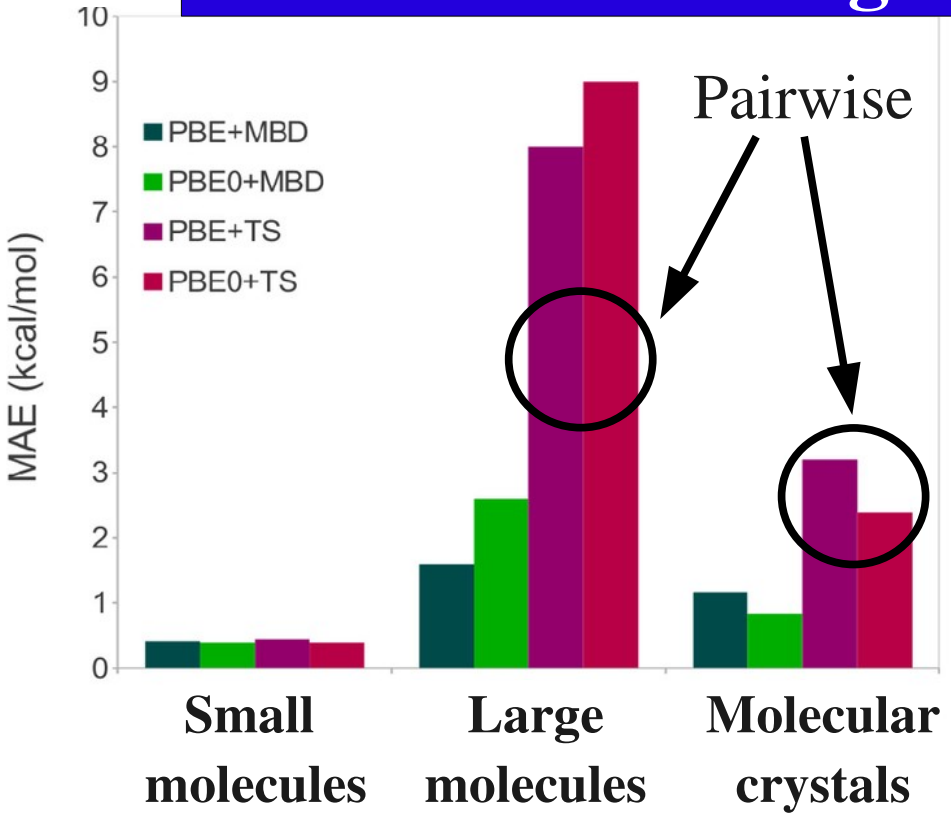


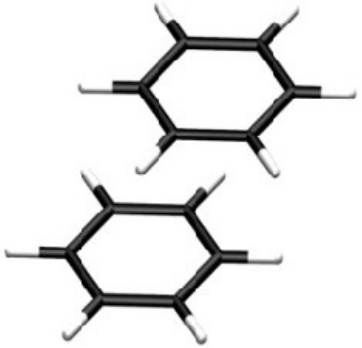
O. A. von Lilienfeld
(U. Basel)

Robert DiStasio Jr.
(Princeton)

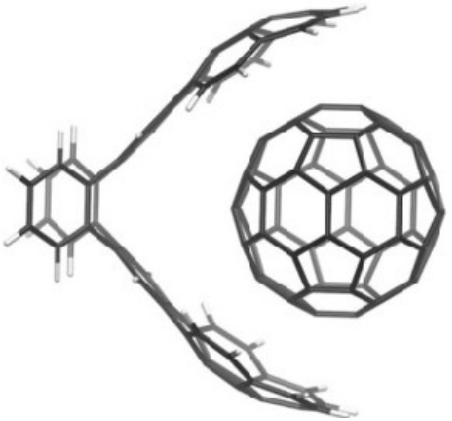
R. A. DiStasio Jr., O. A. von Lilienfeld, and A. Tkatchenko, ***PNAS*** (2012)

Performance of DFT+MBD for interaction energies in molecular materials

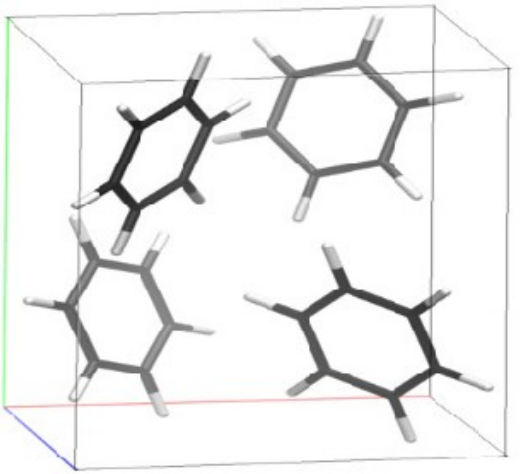




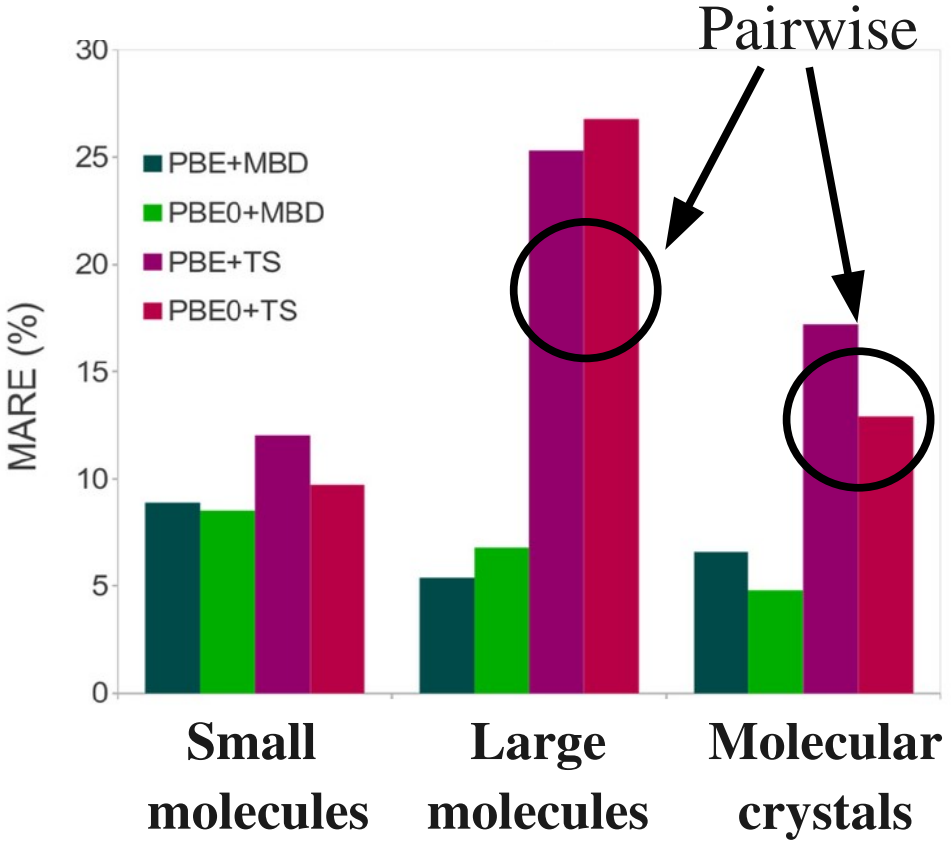
528 dimers



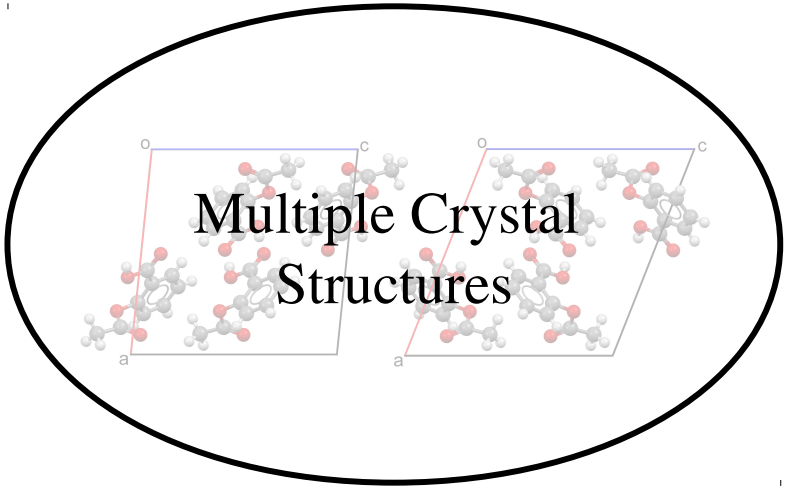
12 dimers



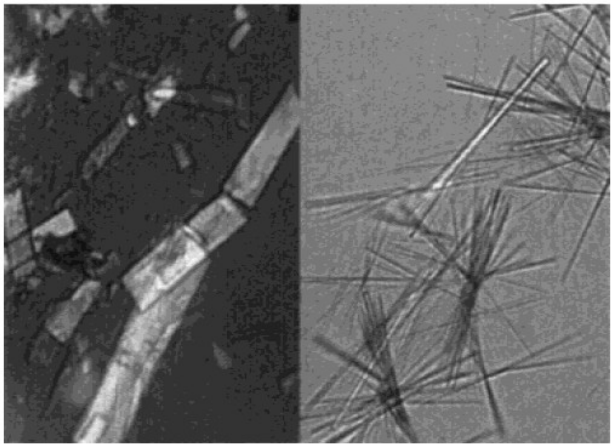
23 crystals



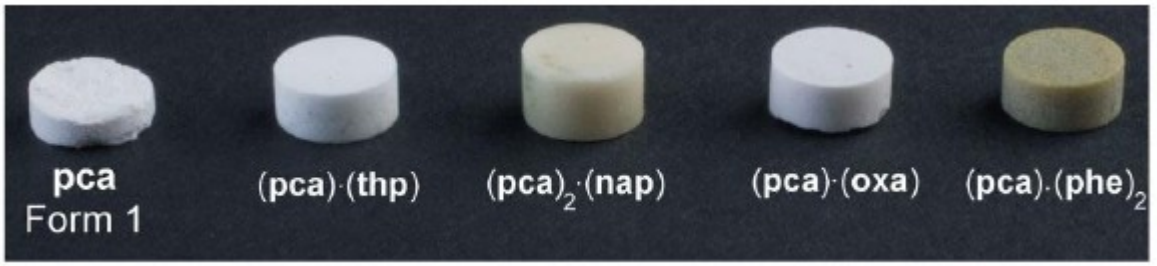
Many-body effects play a qualitative role:
Polymorphism in molecular crystals



Ritonavir:
"drug gone bad"

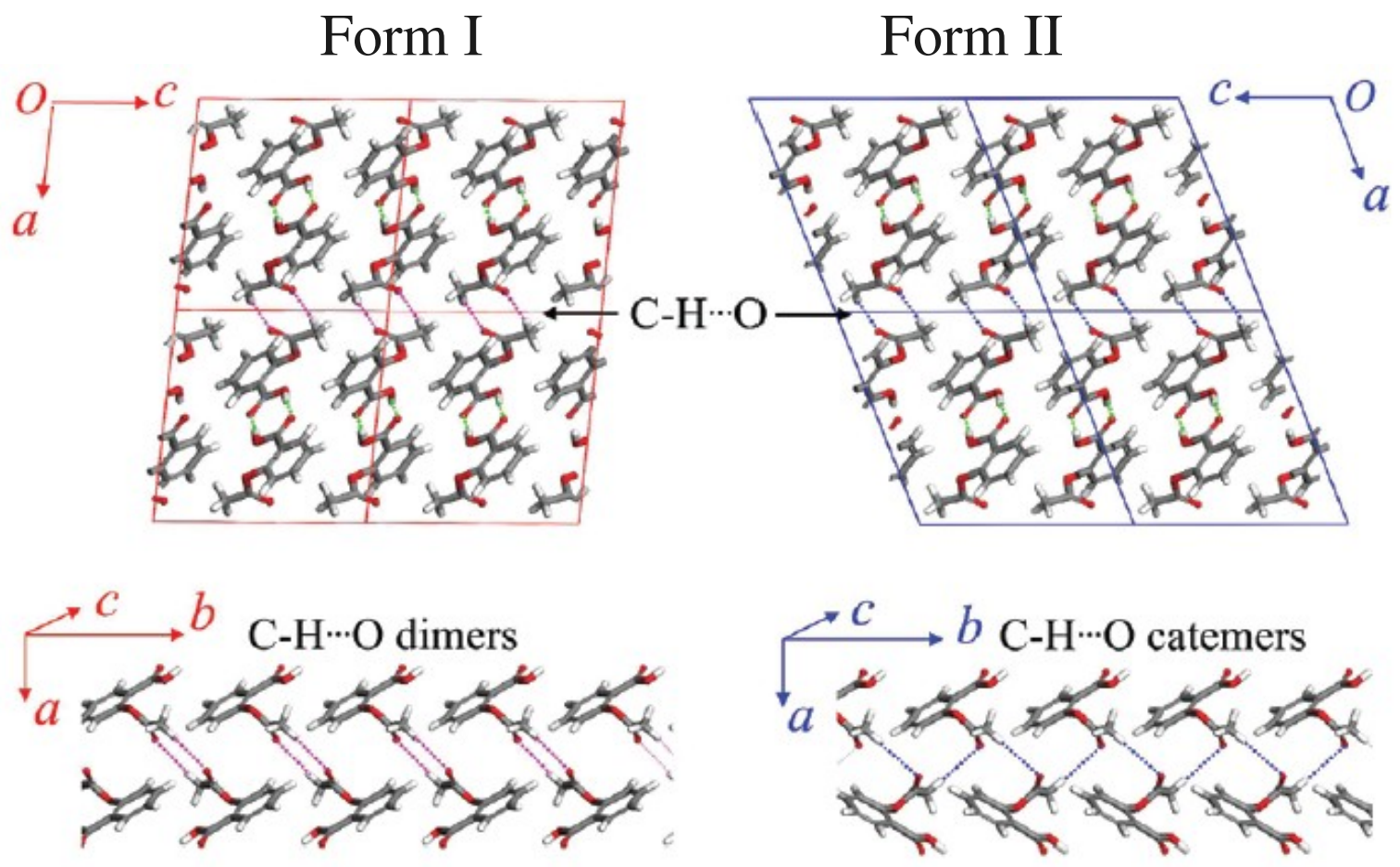


Different mechanical and optical responses,
bio-availabilities *etc*.



Many-body effects in Aspirin

Aspirin crystal



Anthony Reilly

C. Ouvrard and S. L. Price, ***Cryst. Growth Des.*** (2004).

A. D. Bond, R. Boese, G. R. Desiraju, ***Angew. Chem. Int. Ed.*** (2007).

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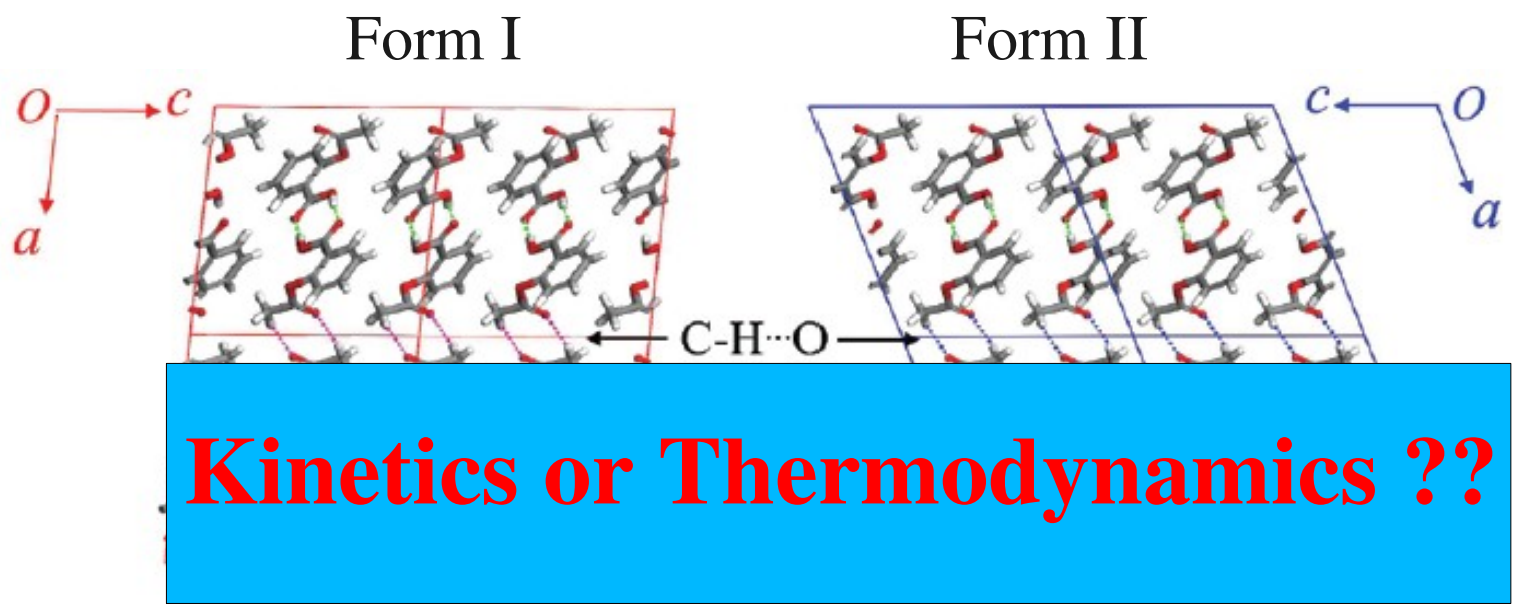
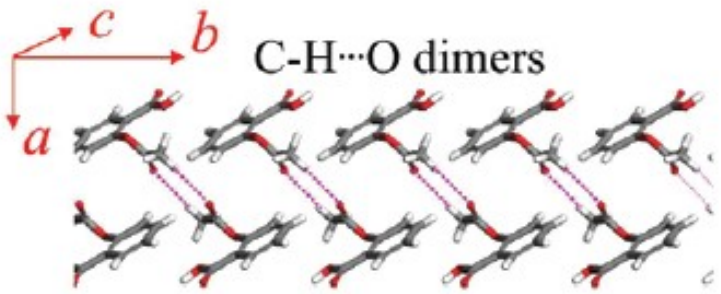
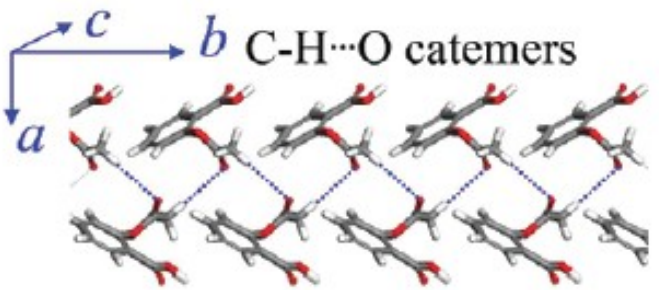


Kinetics or Thermodynamics ??





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Thermodynamics of Aspirin

Lattice energy difference between form I and II
(positive means form I is more stable, in kJ/mol)

PBE+TS	-0.18
PBE+TS+ZPE	-0.42

PBE+MBD	0.04
PBE+MBD+ZPE	0.35

Both polymorphs of aspirin are degenerate ?!

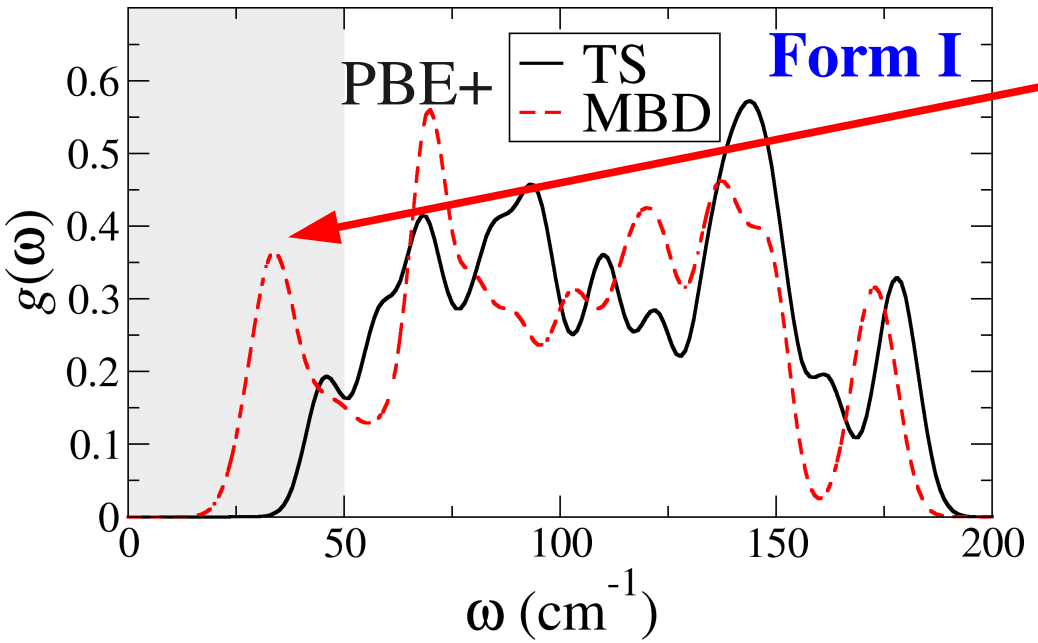
Free Energy in Aspirin: Dynamic Plasmon-Phonon Coupling

Free energy difference between form I and II

(positive means form I is more stable, in kJ/mol)

PBE+TS	-0.18
PBE+TS+ZPE	-0.42
PBE+TS+F_{vib}(298K)	-0.68

PBE+MBD	0.04
PBE+MBD+ZPE	0.35
PBE+MBD+F_{vib}(298K)	**2.56**



A. M. Reilly and A. Tkatchenko, ***Phys. Rev. Lett.***, in print (2014).

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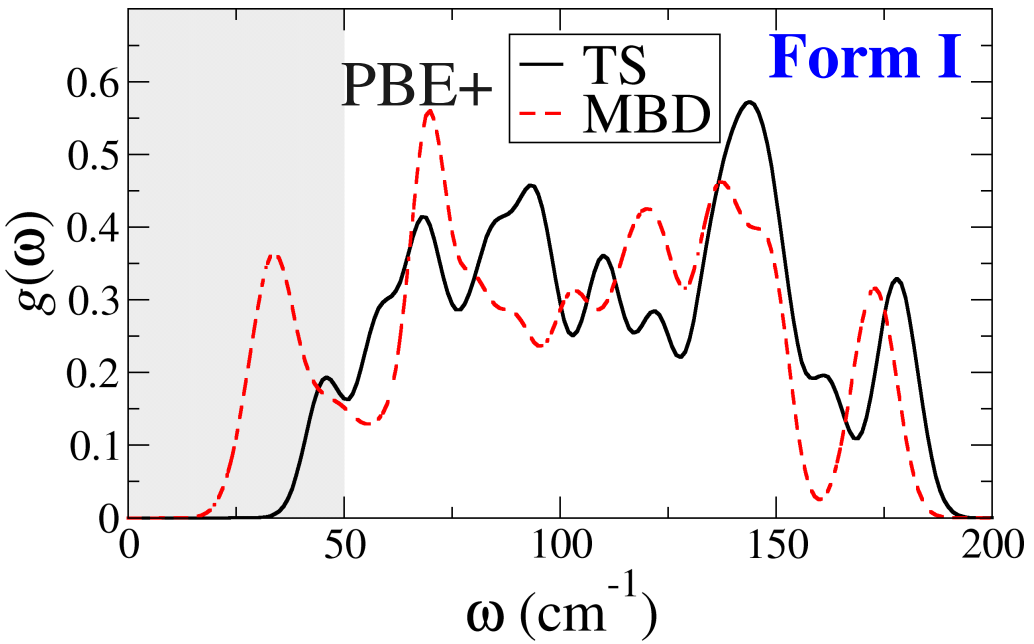
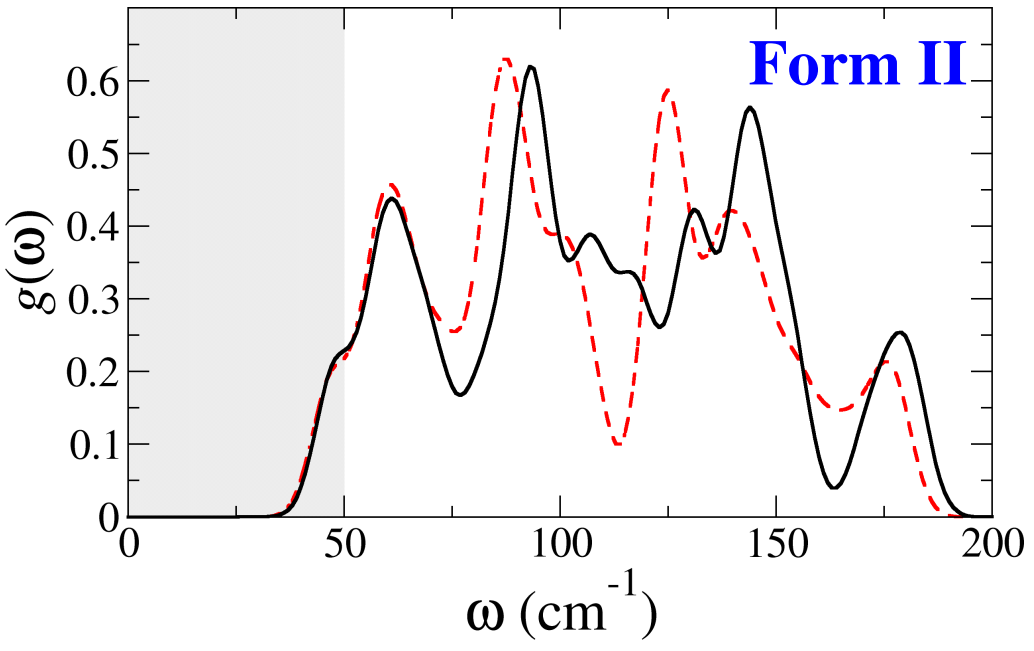
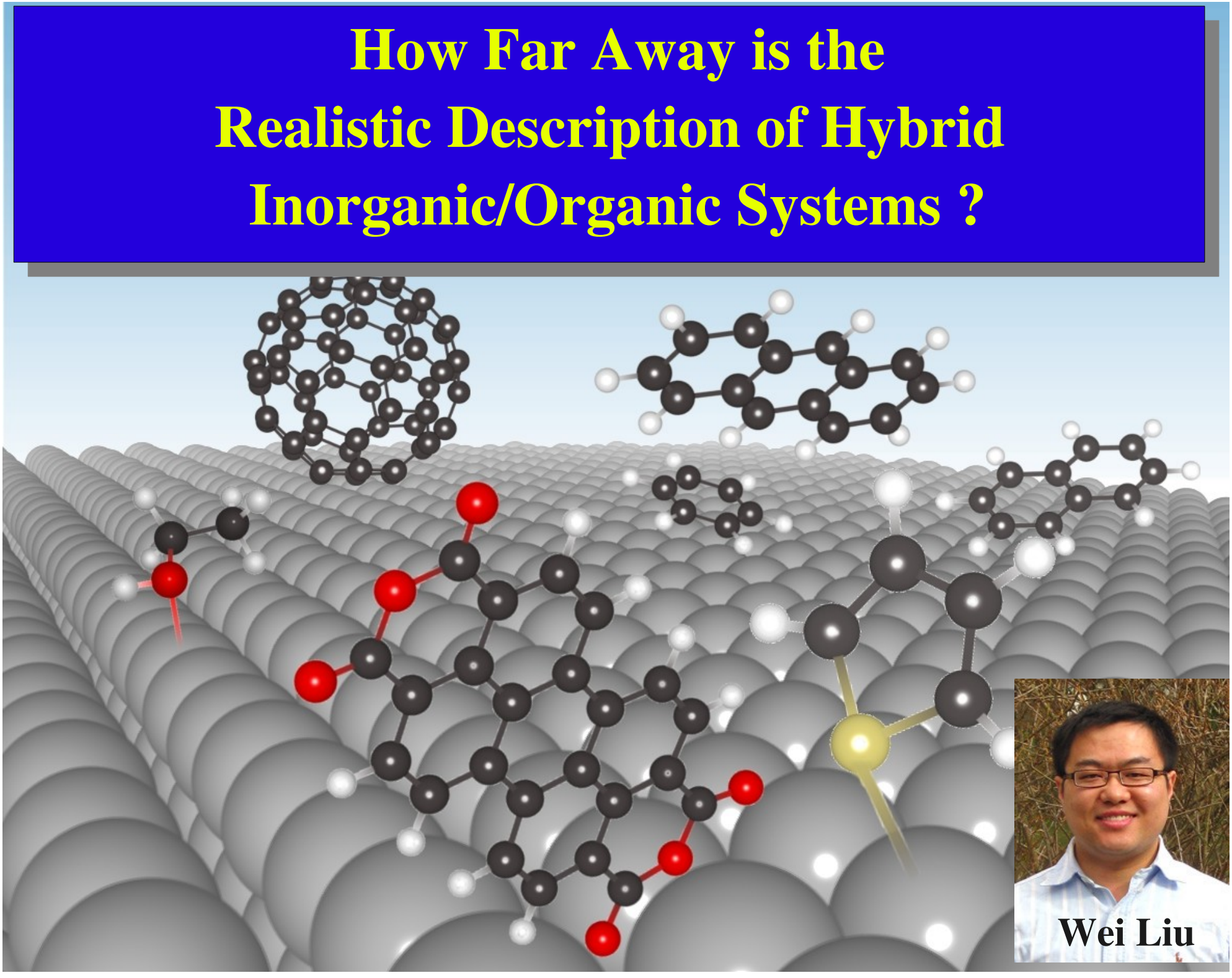




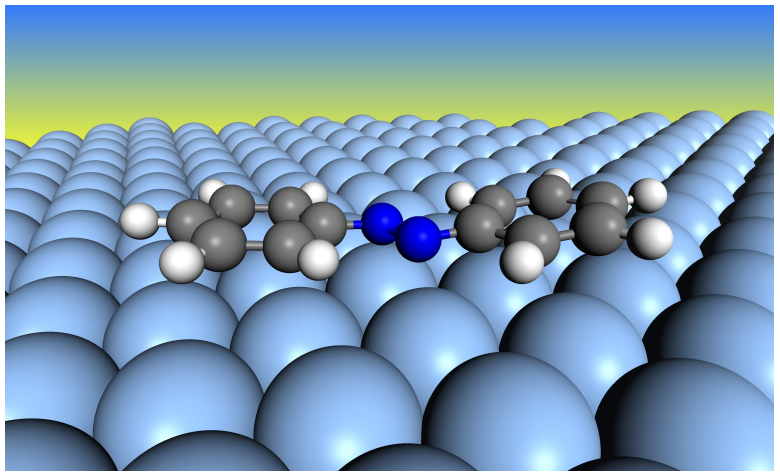
How Far Away is the Realistic Description of Hybrid Inorganic/Organic Systems ?

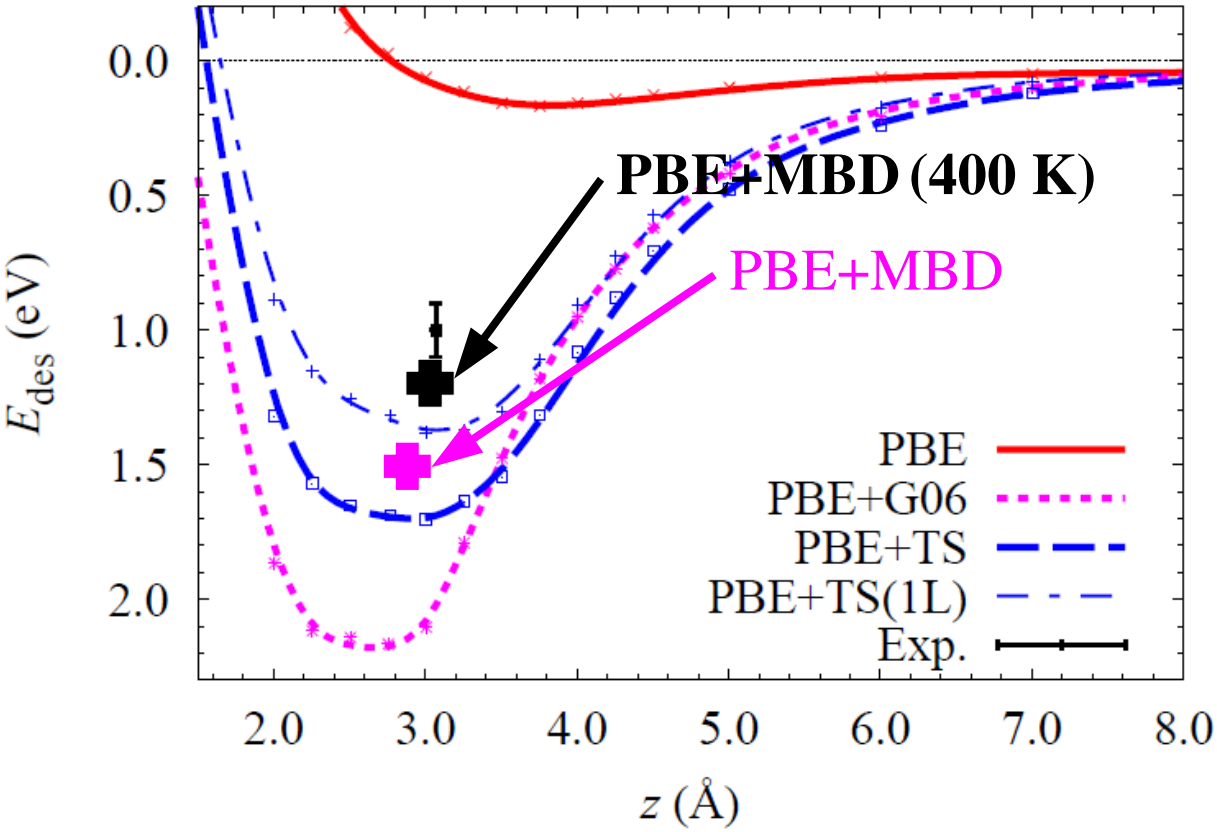


Wei Liu

How Far Away is the Realistic Description of Hybrid Inorganic/Organic Systems ?

Trans-Azobenzene@Ag(111)





G. Mercurio, E.R. McNellis, I. Martin, S. Hagen, F. Leyssner, S. Soubatch, J. Meyer, M. Wolf, P. Tegeder, F.S. Tautz, and K. Reuter, ***Phys. Rev. Lett.*** (2010).

Many-Body Dispersion Interactions:
There is plenty of room at the bottom

Van der Waals correlations are "weak", but ubiquitous, and of increasing importance in larger (heterogeneous) systems

Long list of important properties beyond energies:

- Electronic (dipole, multipoles, charge transfer, …)
- Optical (absorption/reflection spectra, excitons, …)
- Vibrational (THz and IR phonons, polarons, ...)
- Mechanical (bulk modulus, elastic constants, …)
- Novel coupling mechanisms: dynamic plasmon-phonon in aspirin

…

The Many-Body Path Towards Quantitative Modeling of Complex Materials

Explicit (efficient!) many-body methods are crucial for general treatment of collective electronic effects in large molecules and condensed matter, including van der Waals, response properties, ...

These methods can be coupled to (TD)DFT, local-correlation methods, force fields, ...

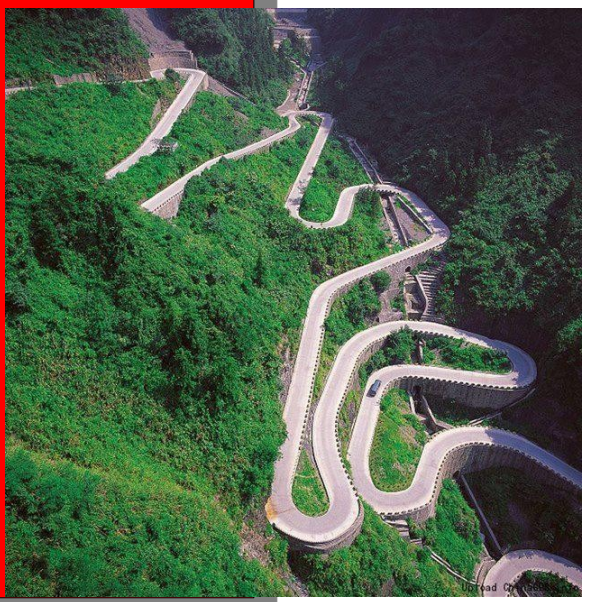
Further necessary work:

Delocalized charge excitations

Relativistic effects (retardation)

Thermal fluctuations, response

Higher multipole effects

Systematic scaling to larger systems

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