When (2 + 2) ≠ 4

or

Van der Waals Interactions in Complex (and Simple) Materials

Alexandre Tkatchenko

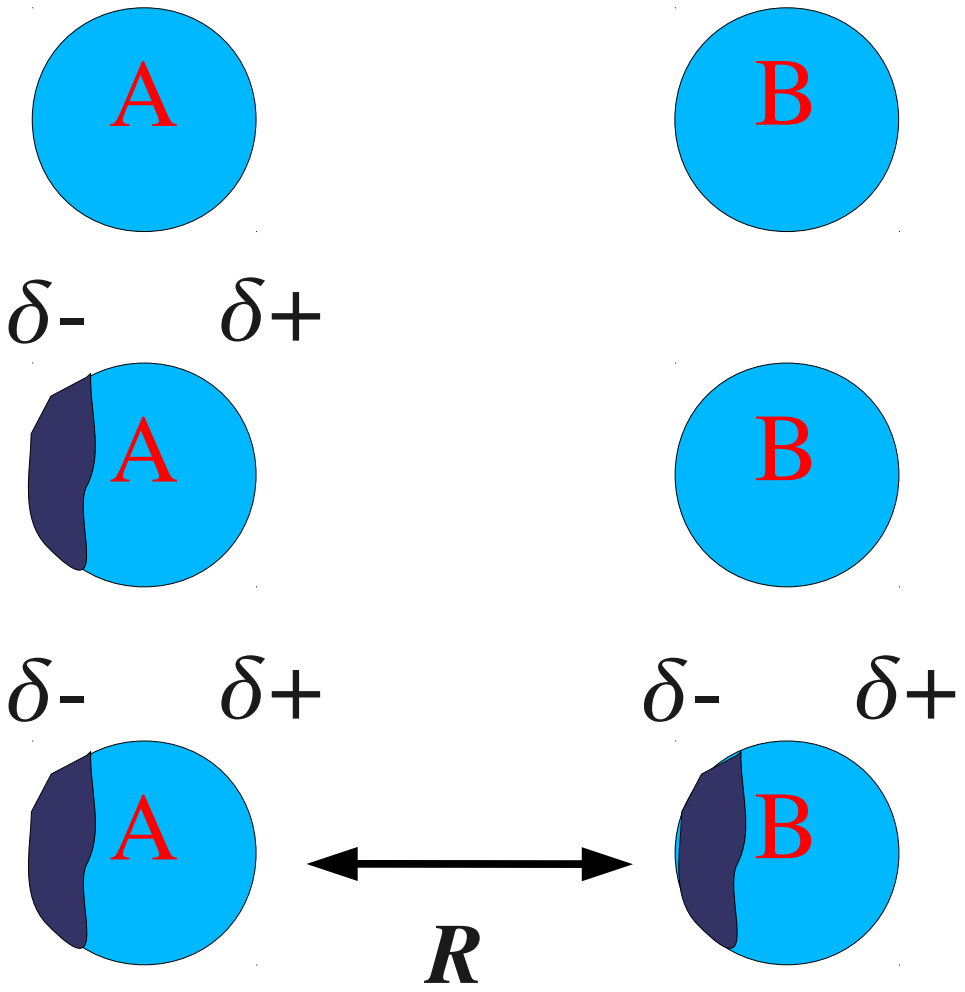
Fritz-Haber-Institut der Max-Planck-Gesellschaft,

Berlin, Germany

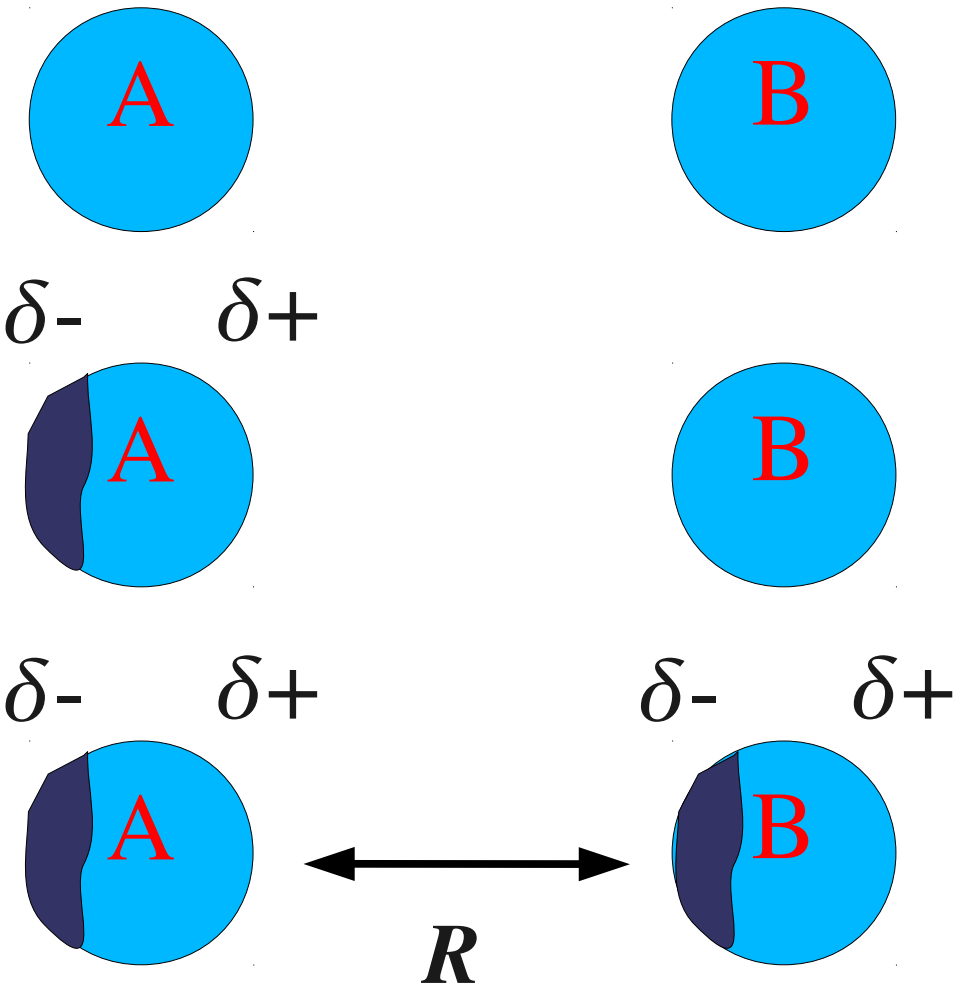
FPCSS2013, Norderney, Jul 25, 2013

Textbook picture of vdW interactions

Textbook picture of vdW interactions

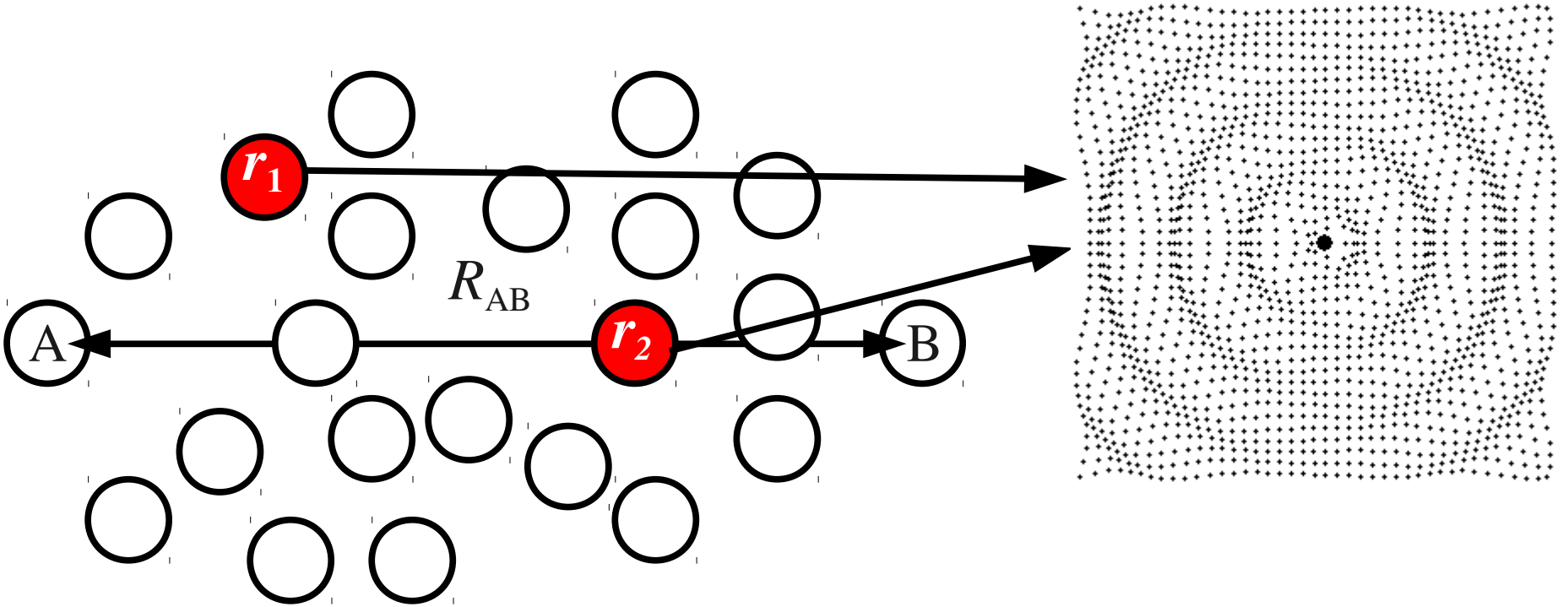


Textbook picture of vdW interactions

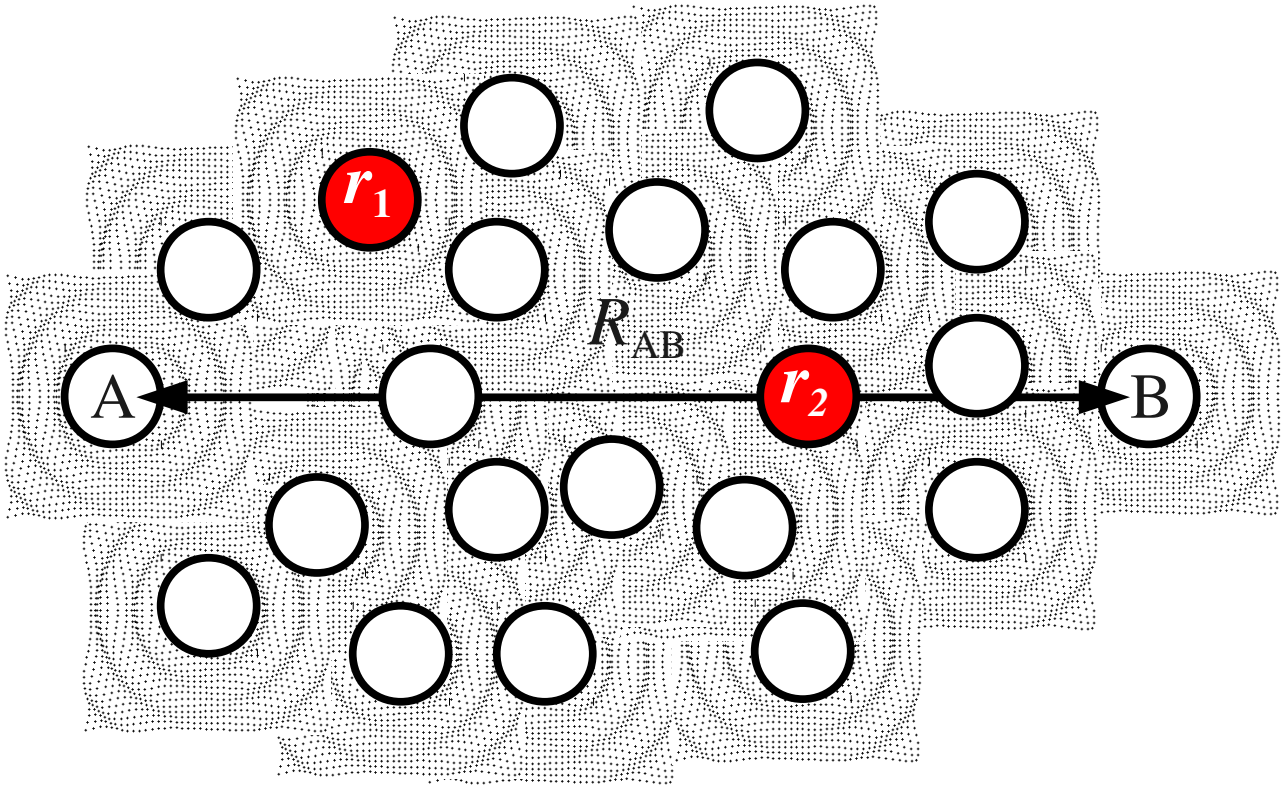


$$E^{(2)}_{\mathrm{vdW}} = -\frac{C_6^{\mathrm{AB}}}{R^6_{\mathrm{AB}}} \rightarrow C_6^{\mathrm{AB}} = \frac{3}{\pi}\int \alpha_{\mathrm{A}}(i\omega)\alpha_{\mathrm{B}}(i\omega)d\omega$$

Beyond textbook model of vdW interactions: Electrodynamic response effects



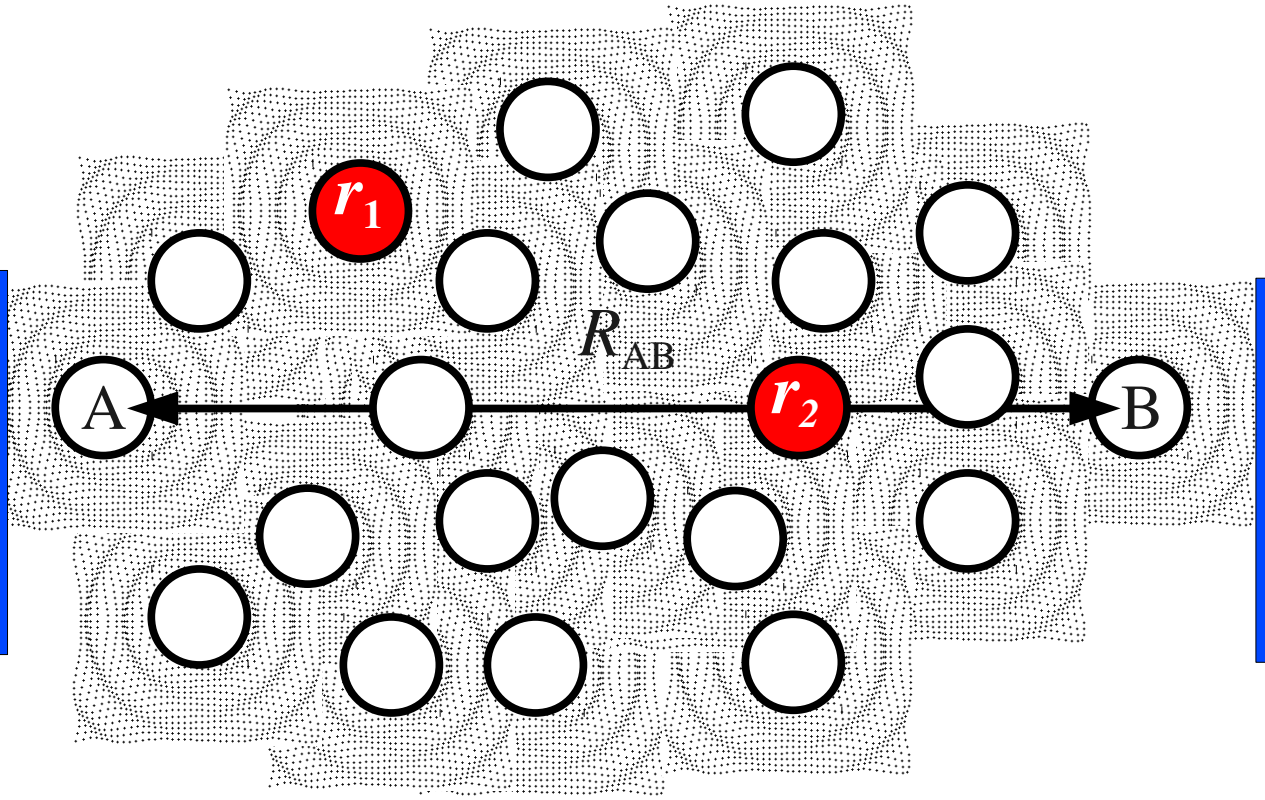
Beyond textbook model of vdW interactions: Electrodynamic response effects



Beyond textbook model of vdW interactions: Electrodynamic response effects

1

Accurate Microscopic Modeling of Coulomb Response



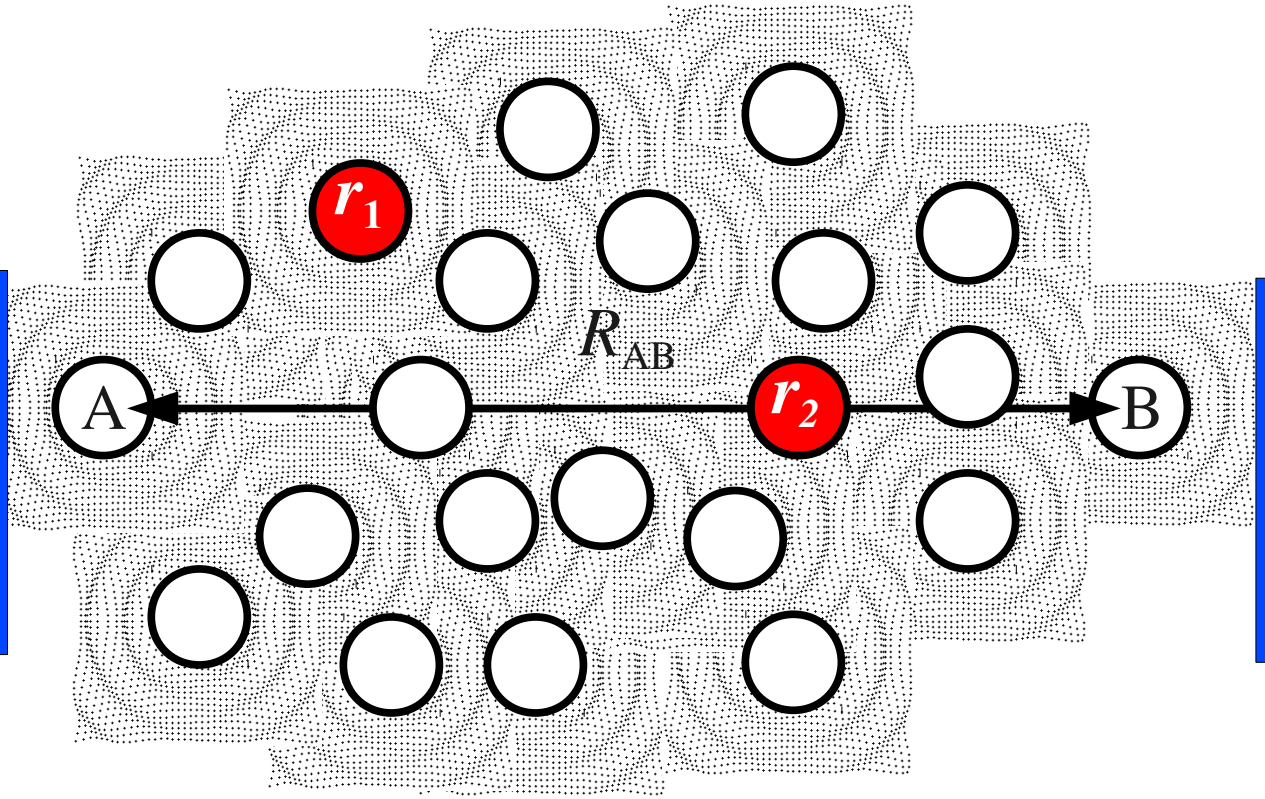
2

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



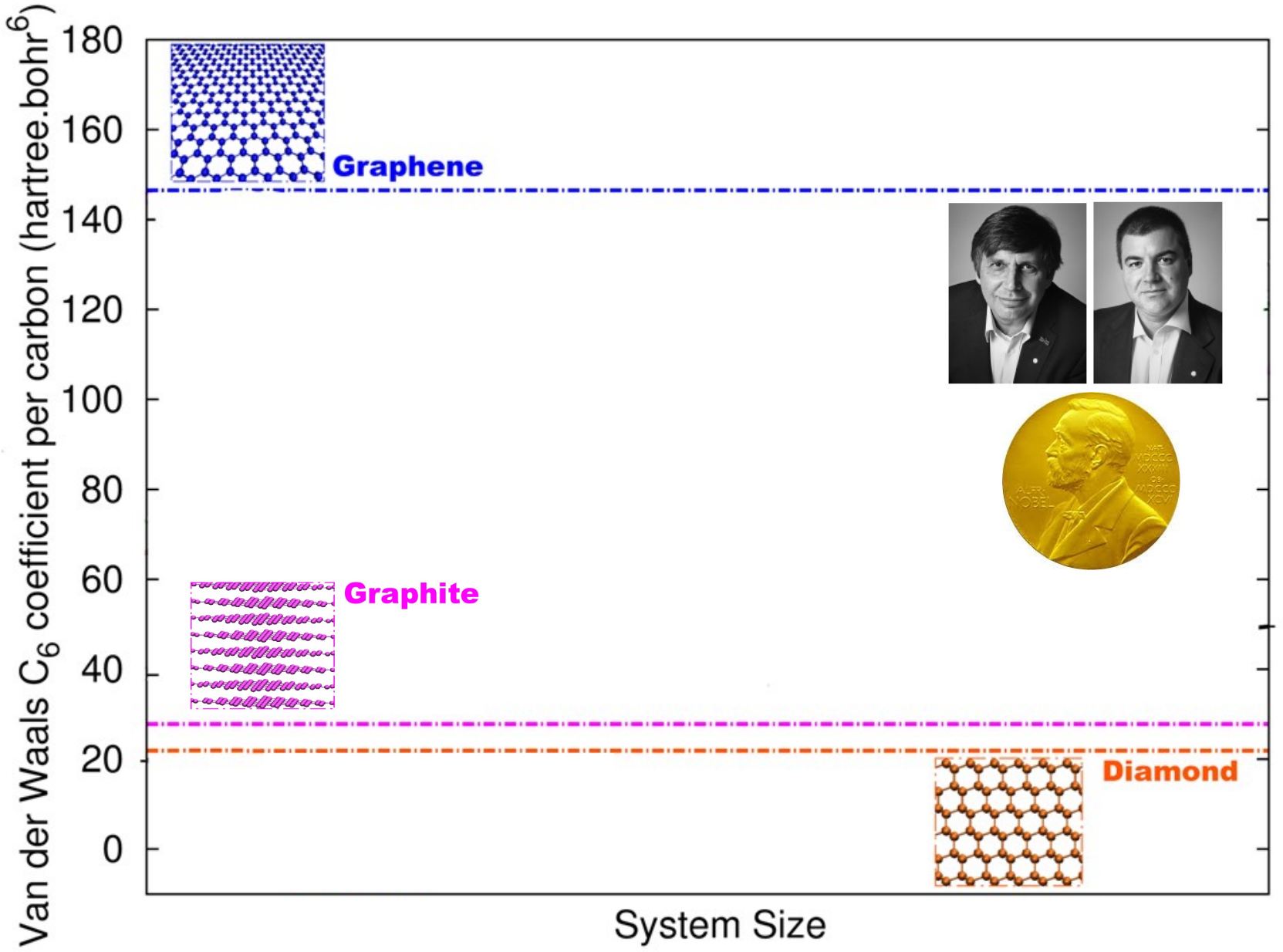
2

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

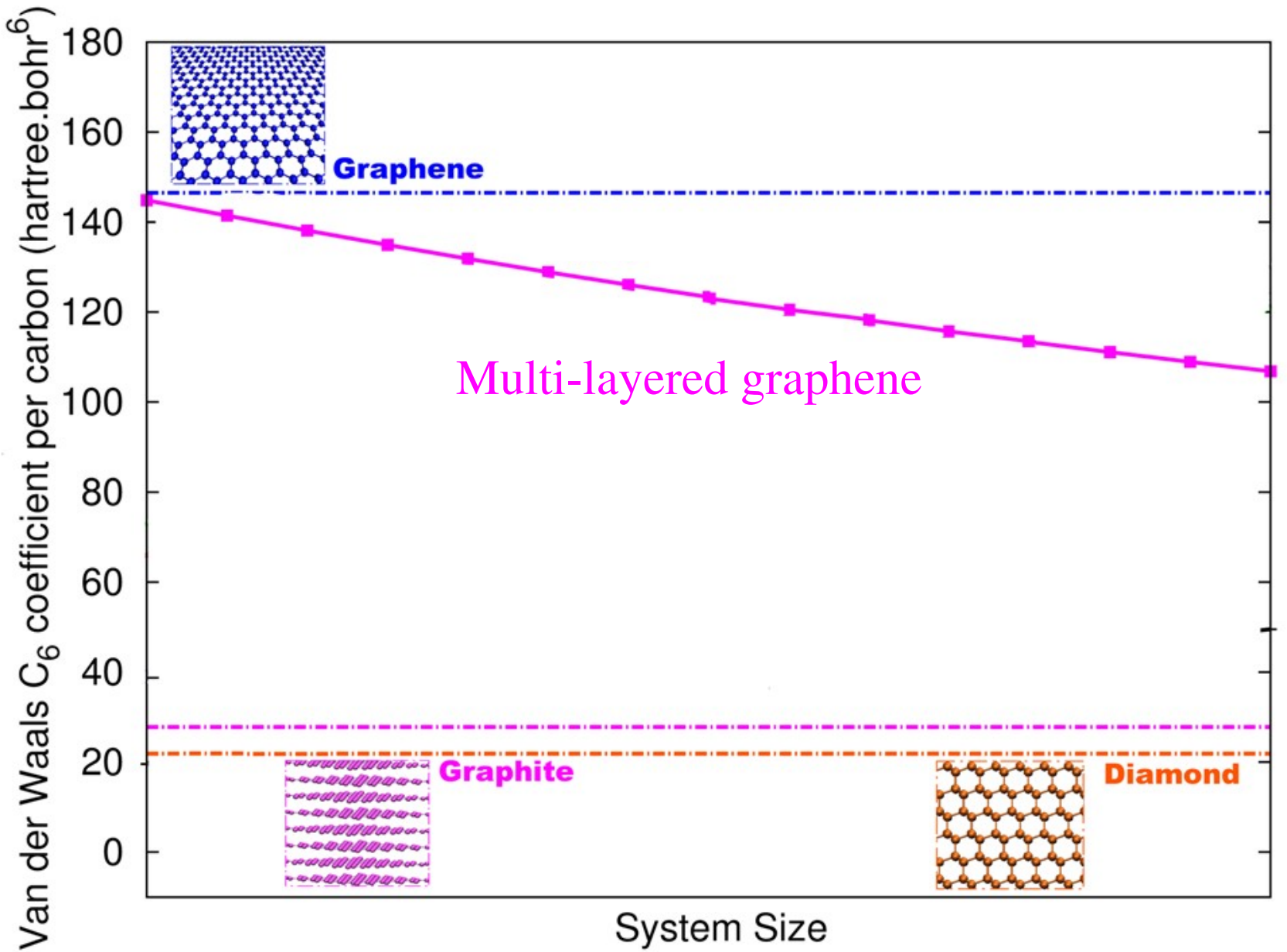
$$E_c = -\int_0^\infty \frac{d\omega}{2\pi}\int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1},\mathbf{r_2};i\omega)-\chi_0(\mathbf{r_1},\mathbf{r_2};i\omega))\frac{1}{|\mathbf{r_1}-\mathbf{r_2}|}\right)$$

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

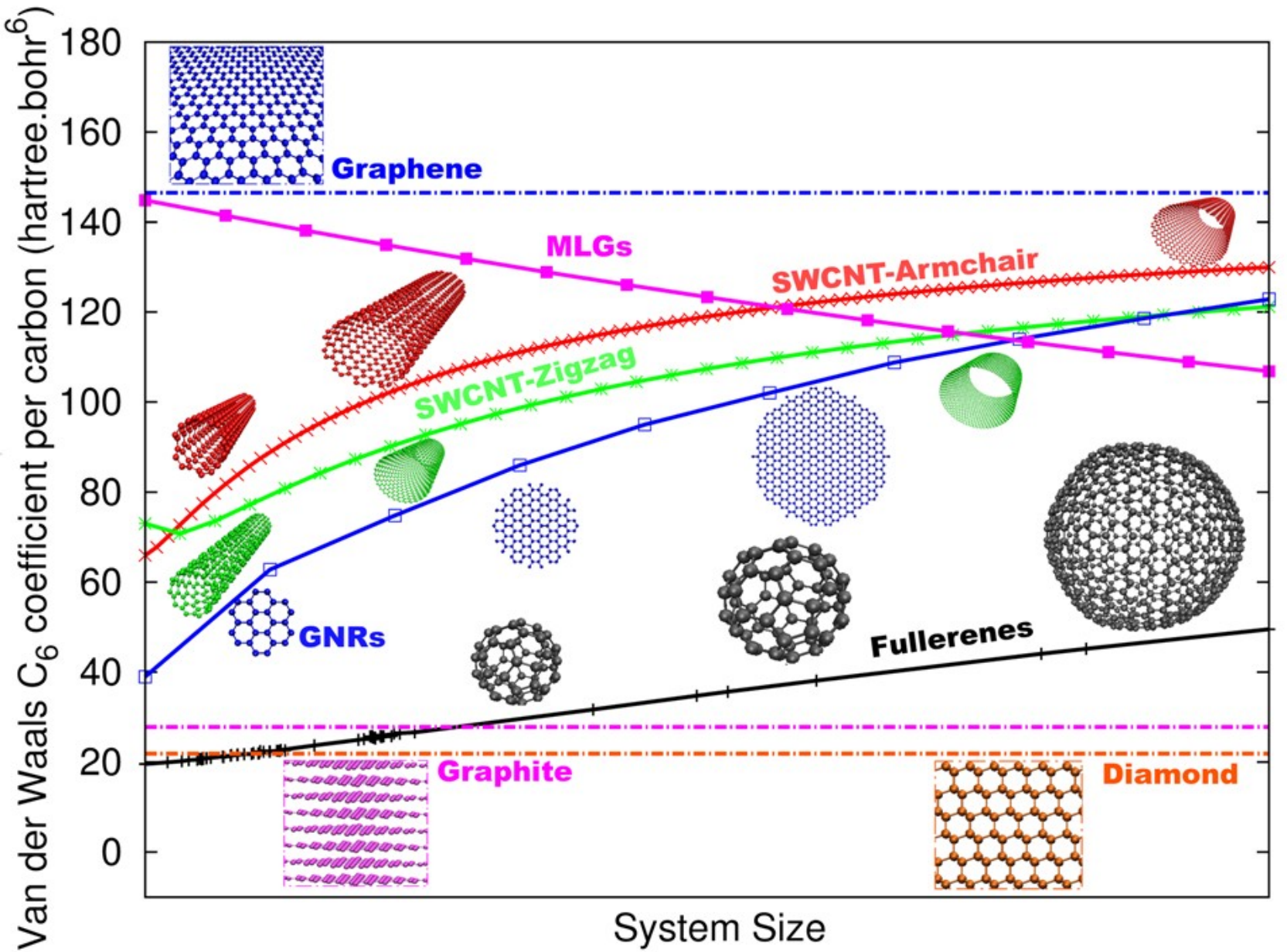
Electrodynamic treatment of vdW interactions: beyond "hybridized atoms"



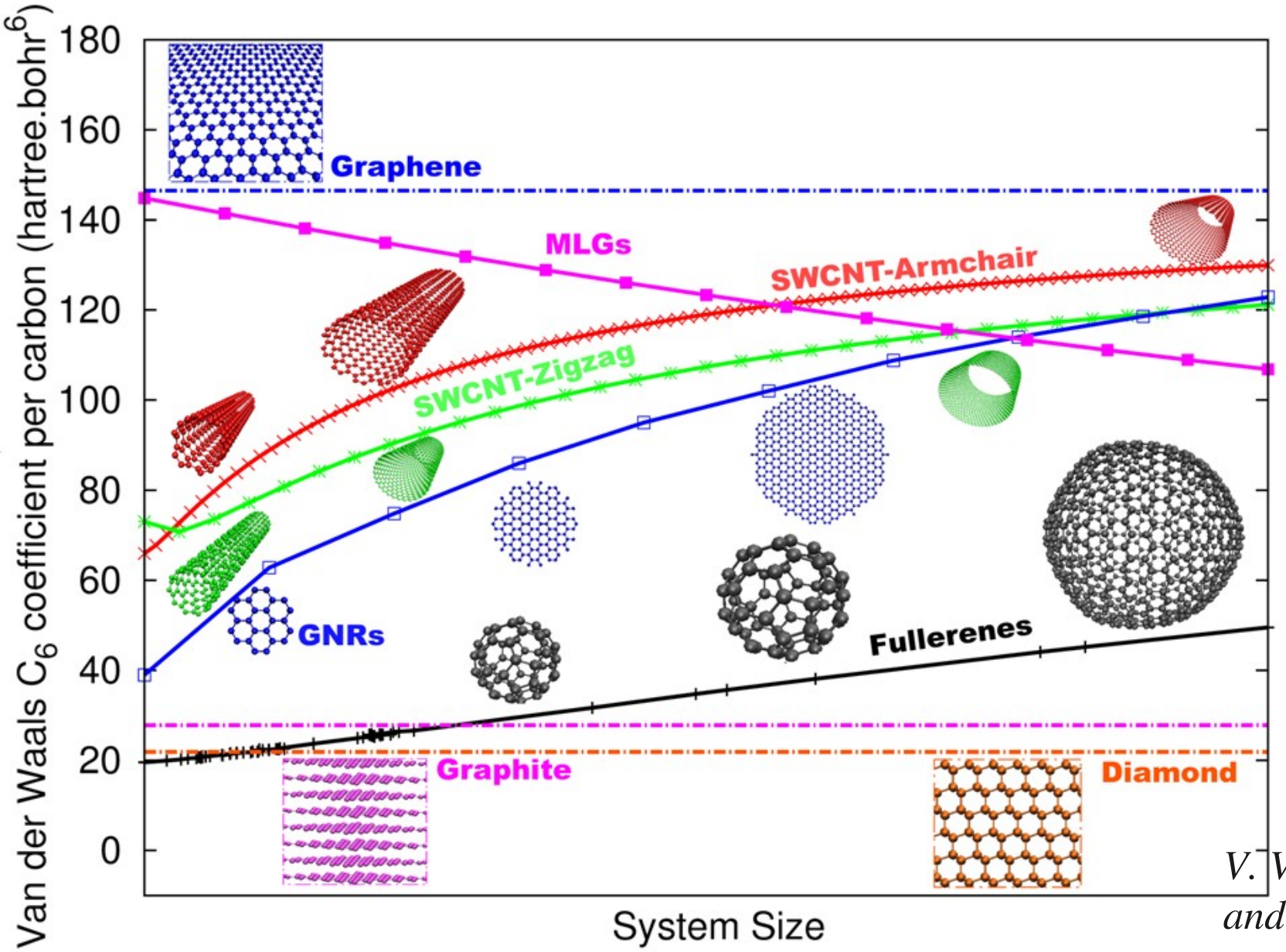
Electrodynamic treatment of vdW interactions: beyond "hybridized atoms"



Electrodynamic treatment of vdW interactions: beyond "hybridized atoms"



Electrodynamic treatment of vdW interactions: beyond "hybridized atoms"



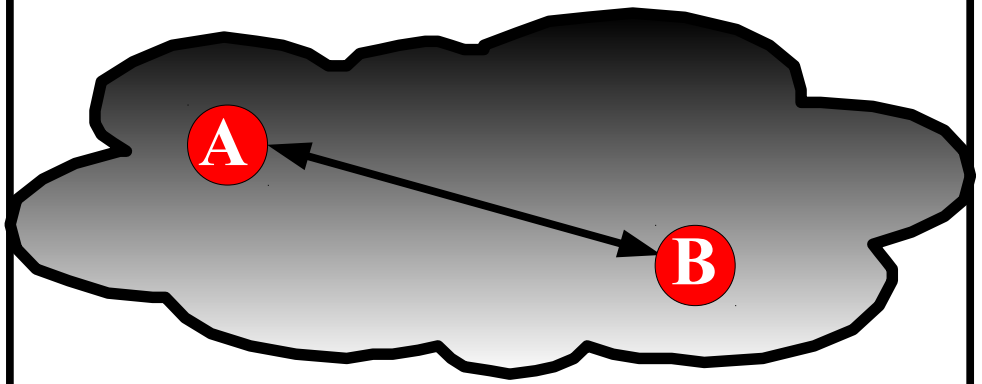
V. V. Gobre and A. Tkatchenko, ***Nature Comm.*** (2013)

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



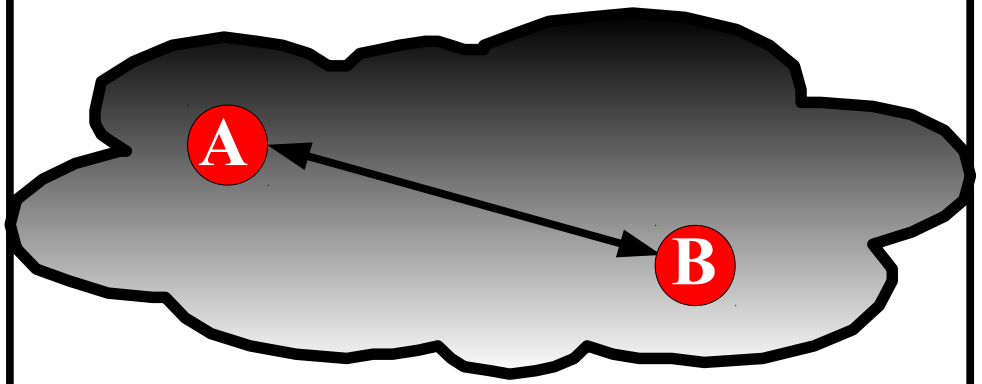
Valid for small molecules ***or*** homogeneous dielectrics

Towards Efficient Many-Body Treatment of vdW Interactions

The conventional approach

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

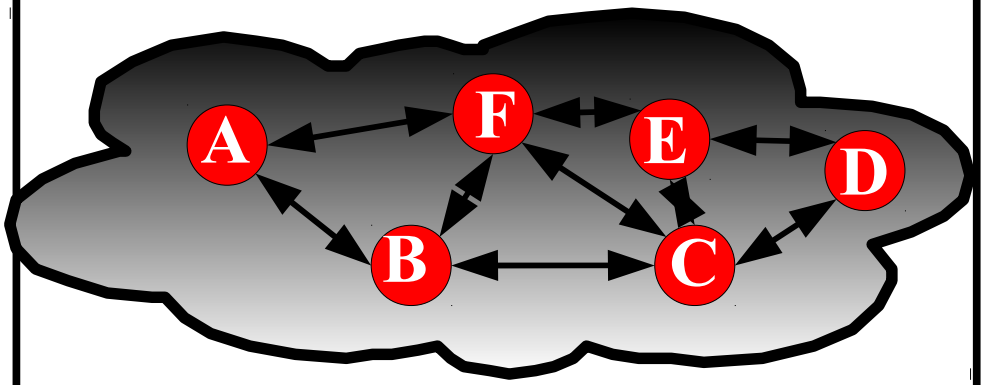
Effective screening and two-body energy



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**)



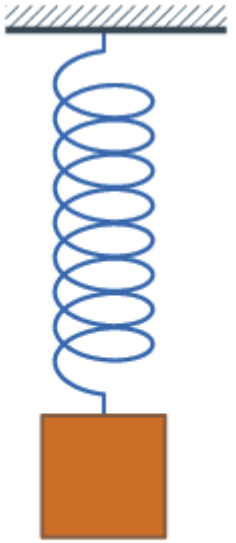
Valid for **small and large molecules, insulators, metals, interfaces, ...**

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)



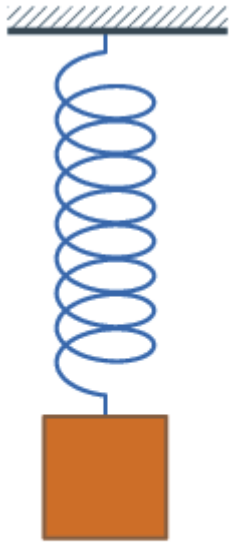
Nucleus (q)

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.

The Model:
Quantum Harmonic Oscillator (QHO)



Nucleus (q)

Harmonic bond (ω)

"Electron" ($-q$,m)

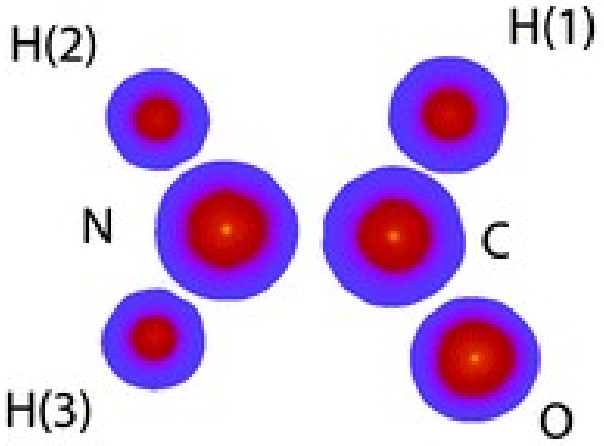
In the dipole approximation:

(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.

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)

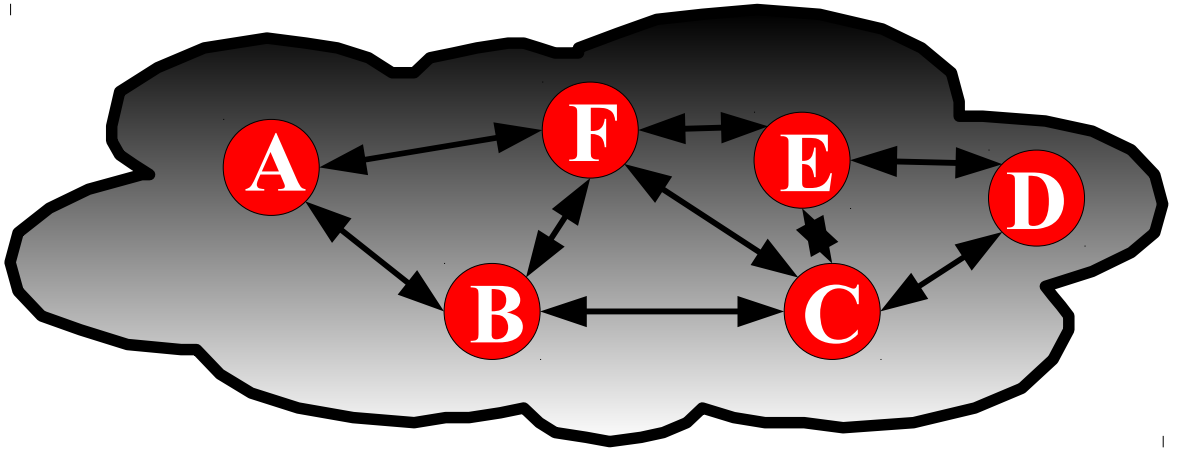
$$\alpha_p(i\omega) = \alpha_p^{\mathrm{TS}}(i\omega) + \alpha_p^{\mathrm{TS}}(i\omega) \sum_{q \neq p}^{N} \mathcal{T}_{pq} \alpha_q(i\omega)$$

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).

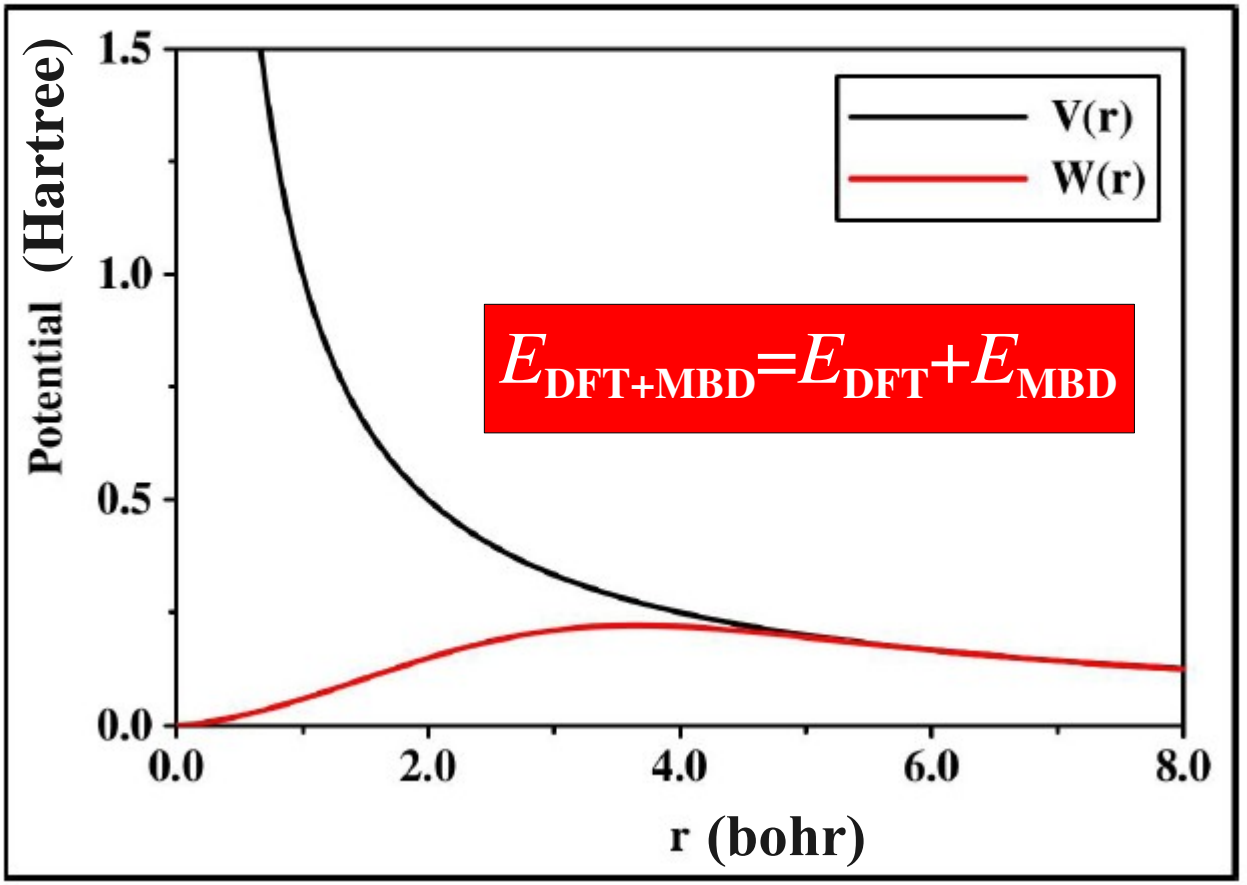
Salient Features of the MBD Method



- 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)

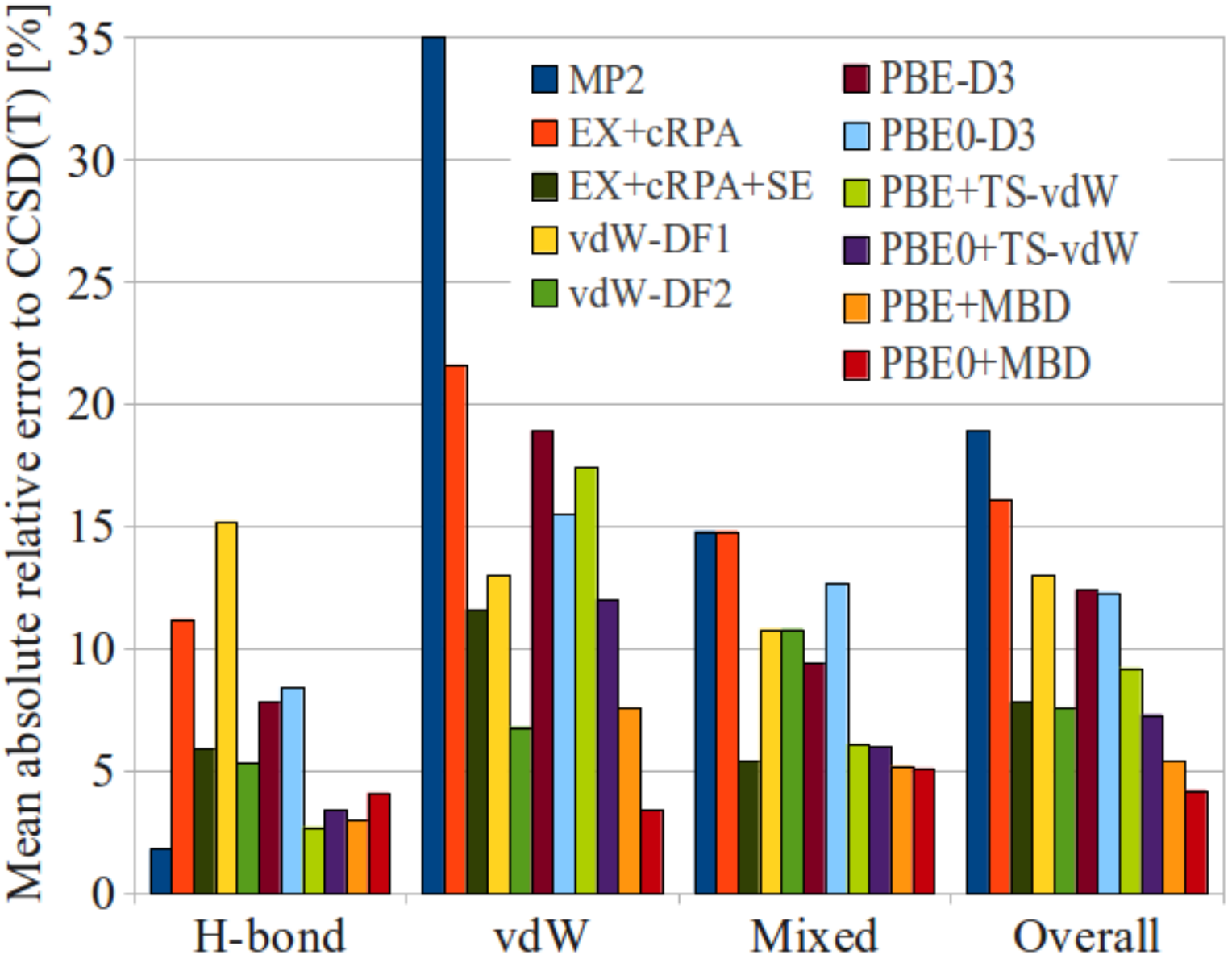
Coupling DFT and MBD by range separation of the Coulomb potential

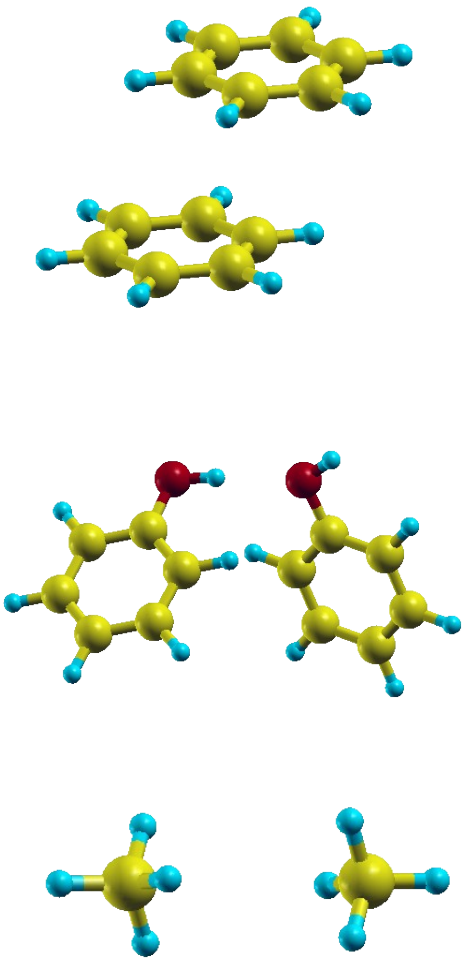
$$W(r_{pq}) = \left(1 - \exp\left(-\left(r_{pq}/R_{pq}^{\mathrm{vdW}}\right)^{\beta}\right)\right)/r_{pq}$$



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

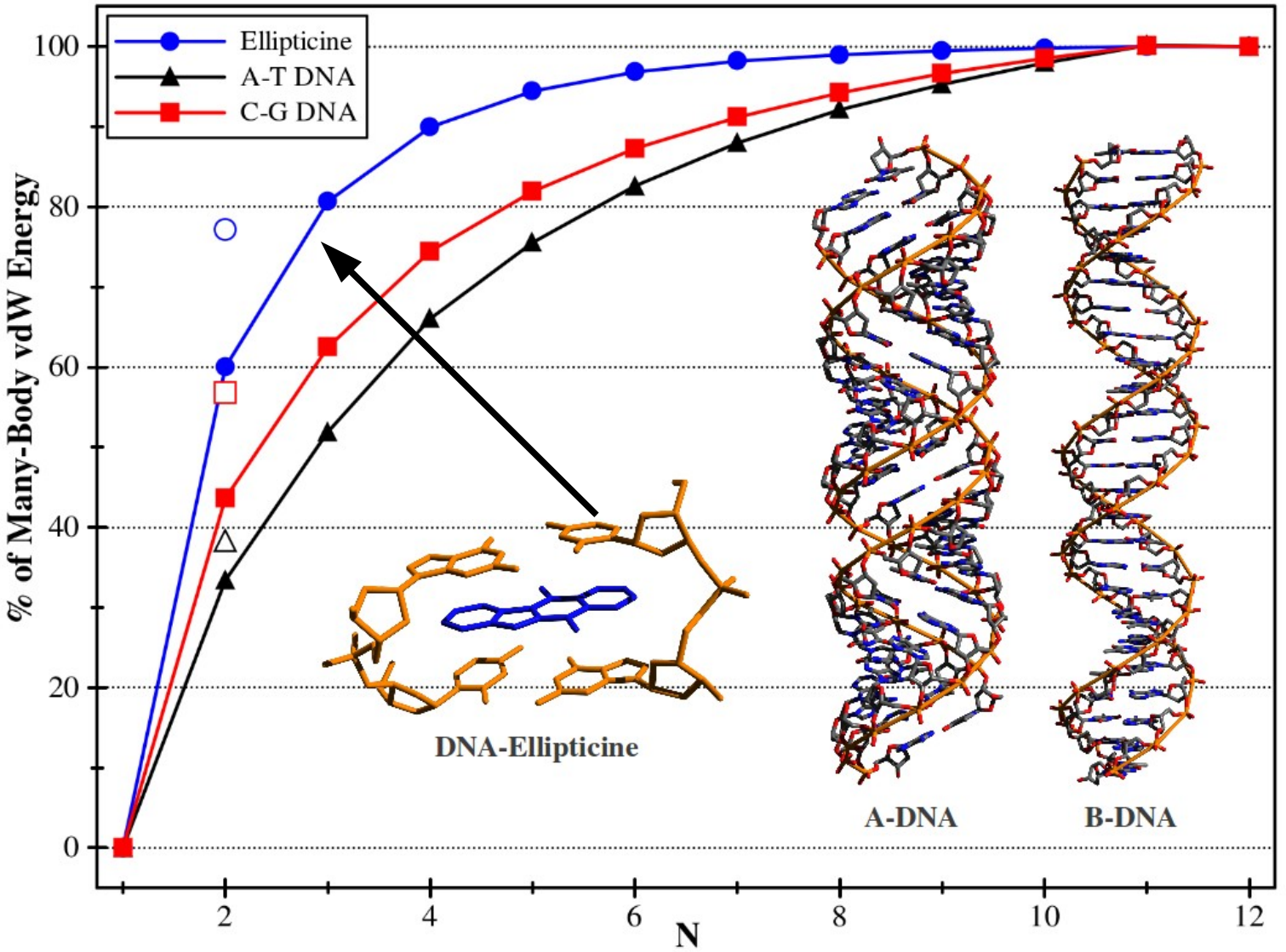
Performance of DFT+MBD for gas-phase intermolecular interactions





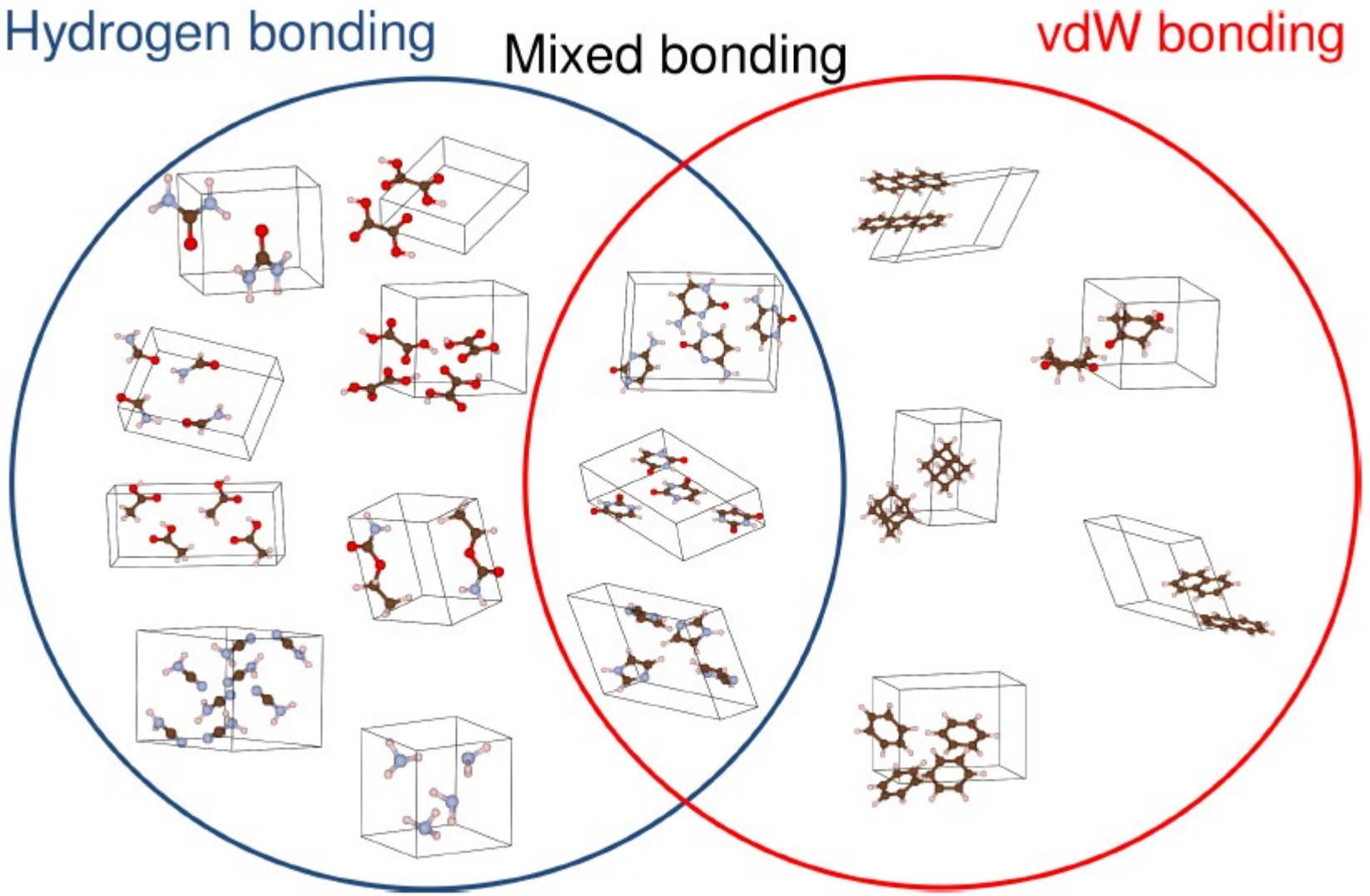
S22 CCSD(T): *Jurecka, Sponer, Cerny, Hobza,* ***PCCP*** (2006); *Sherrill et al.,* ***JCP*** (2010).

Large many-body vdW effects in complex molecular geometries



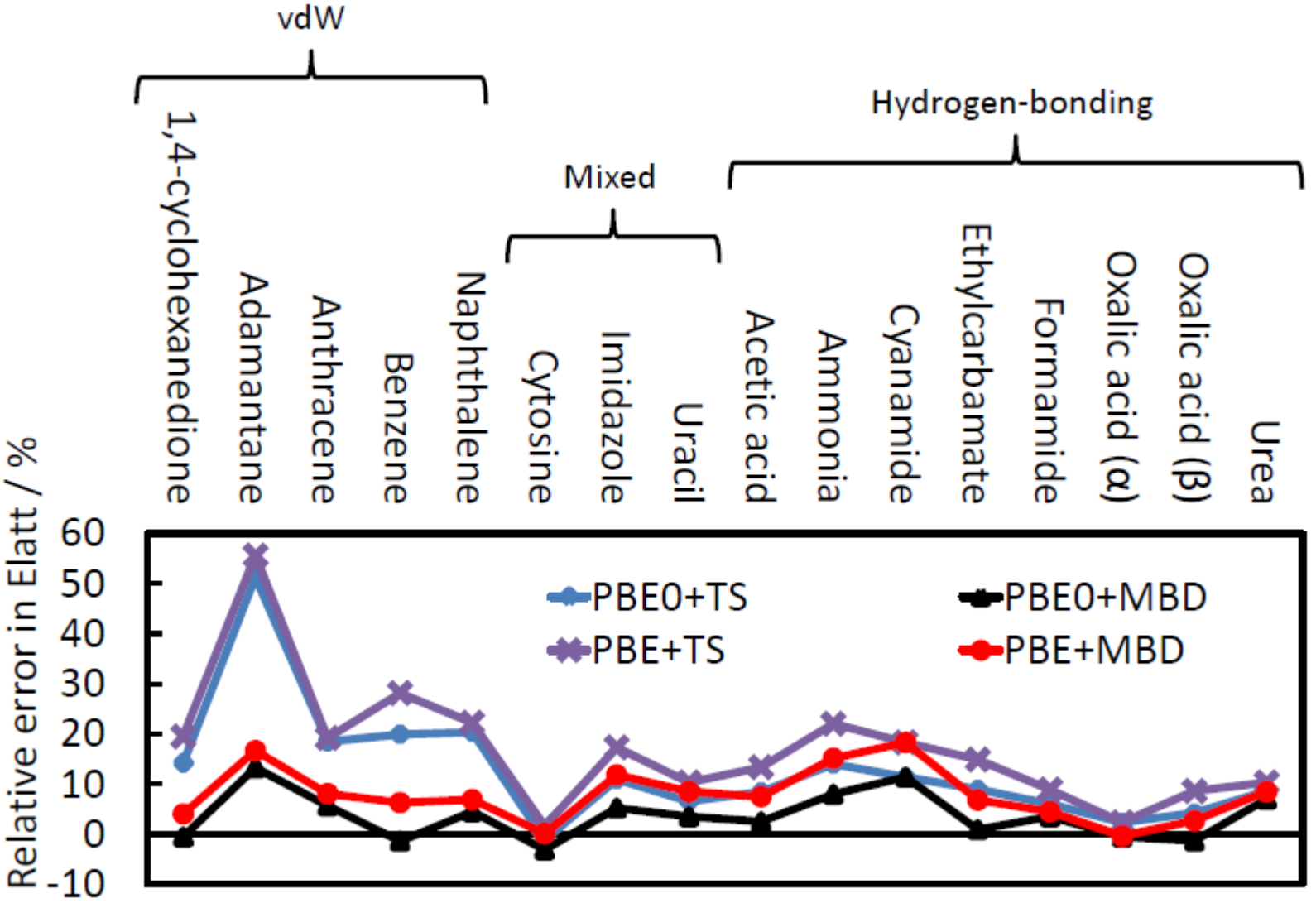
R. A. DiStasio Jr., O. A. von Lilienfeld, and A. Tkatchenko, ***PNAS*** (2012)

"Chemically Accurate" Predictions for Molecular Materials

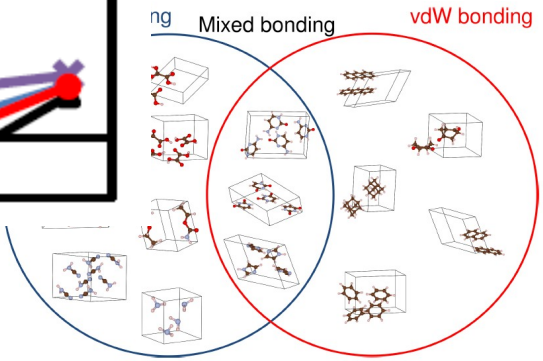


A. M. Reilly and A. Tkatchenko, ***J. Phys. Chem. Lett.*** **4**, 1028 (2013).

"Chemically Accurate" Predictions for Molecular Materials



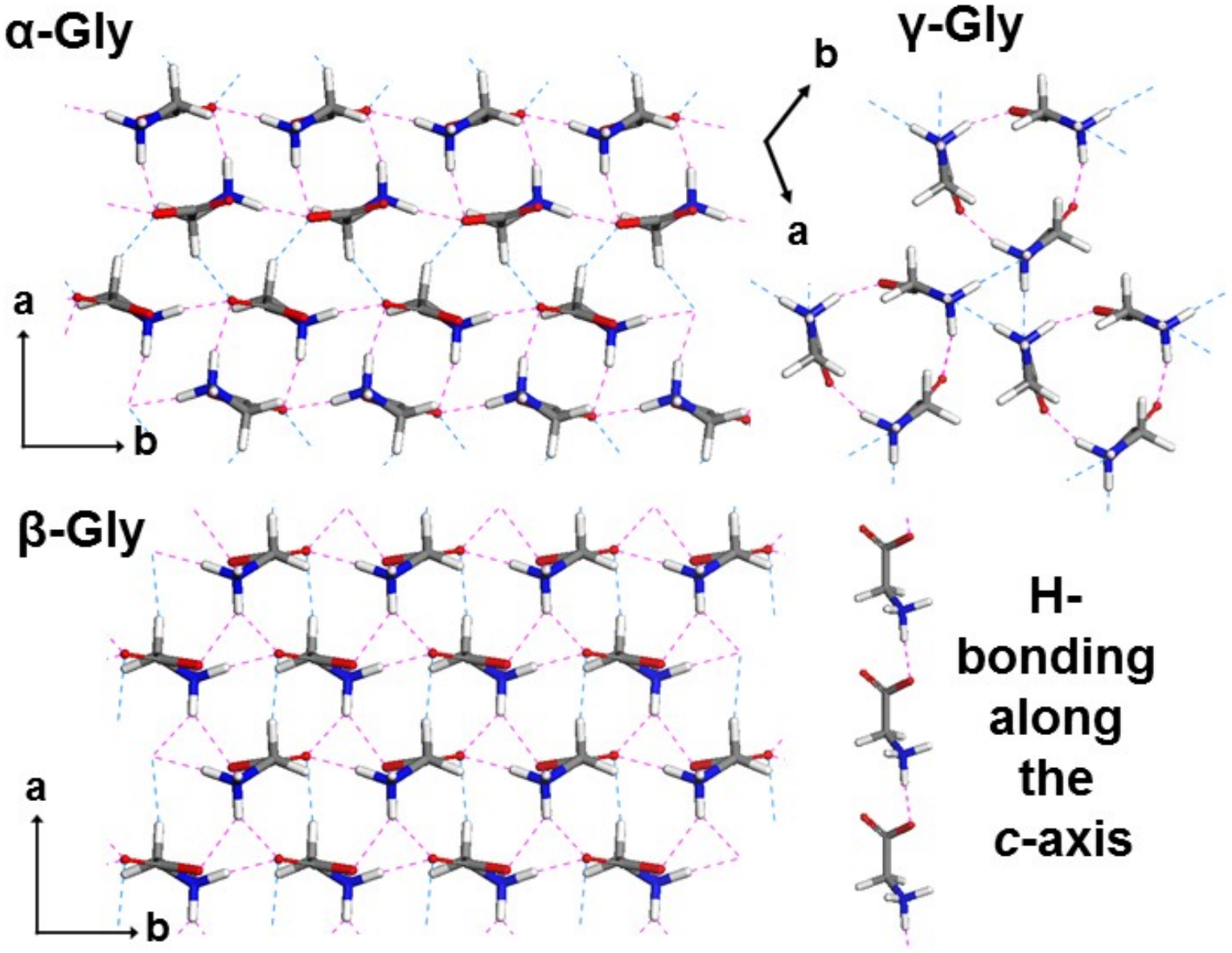
Anthony Reilly



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

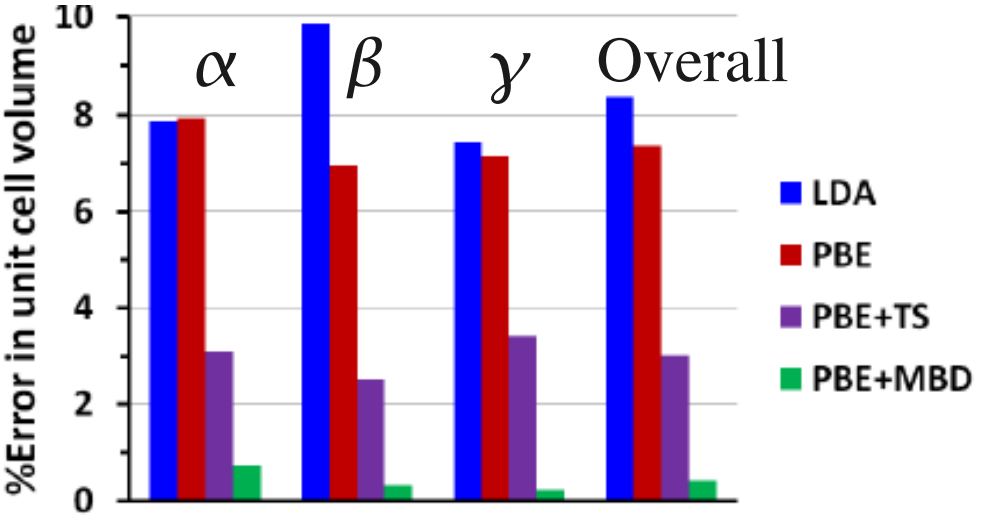
A. M. Reilly and A. Tkatchenko, ***J. Phys. Chem. Lett.*** **4**, 1028 (2013).

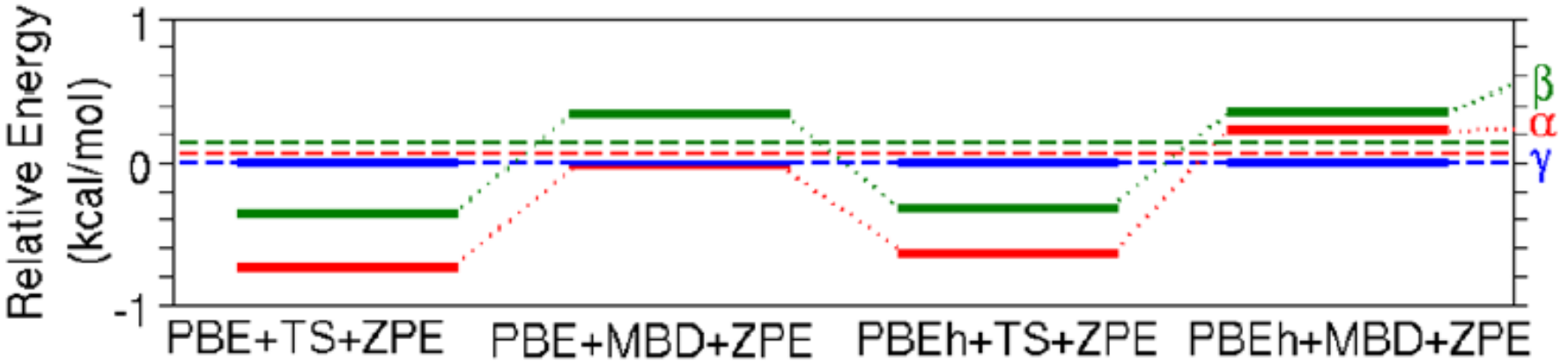
DFT+MBD correctly discriminates between crystal polymorphs: Example of glycine



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

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



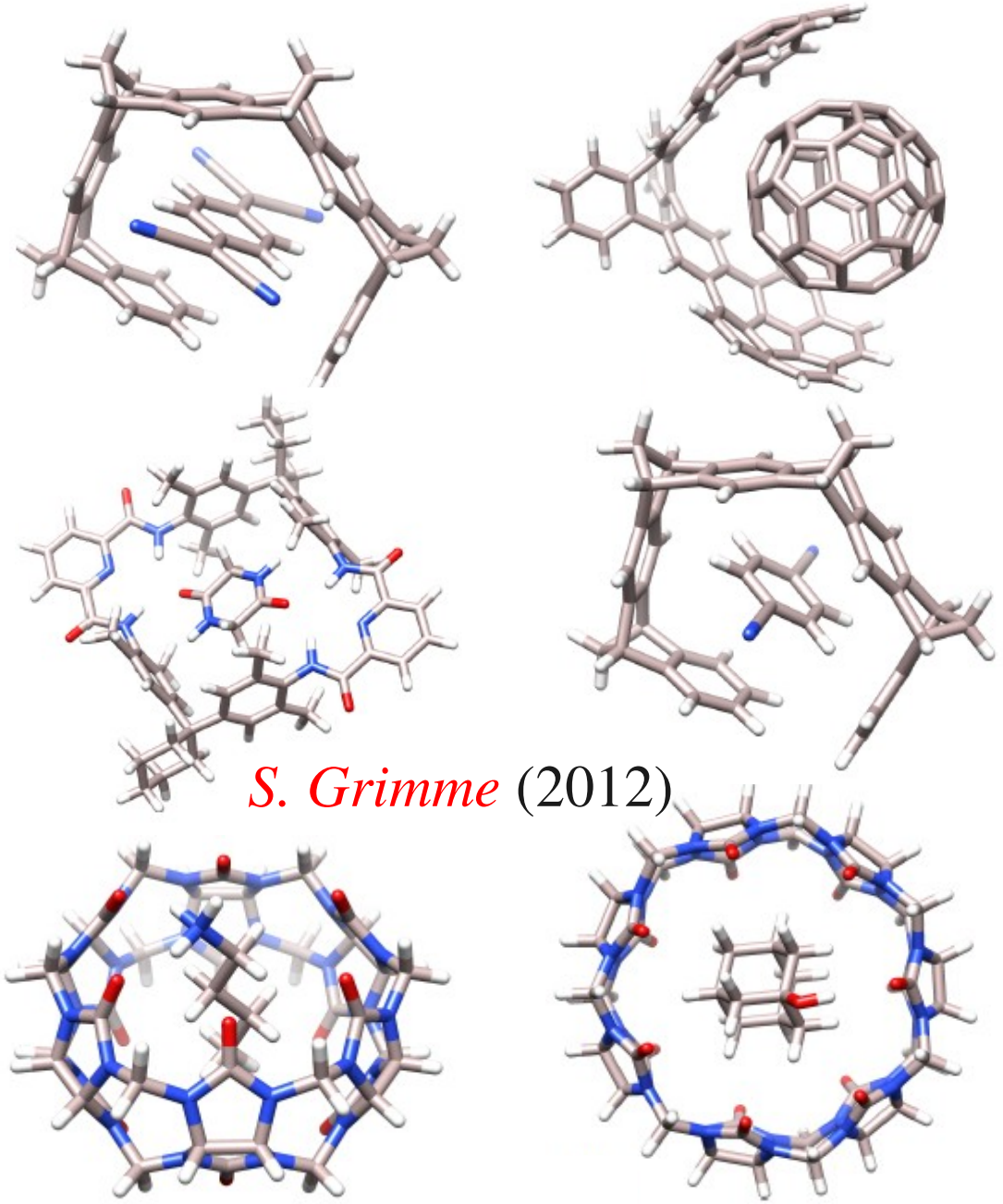


DFT+MBD gives relative energies in excellent agreement with experiment, reaching an accuracy better than 0.3 kcal/mol!

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).

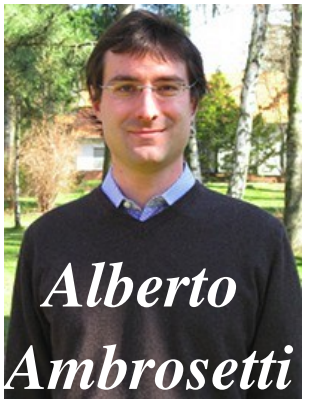
Binding in supramolecular systems: PBE+MBD performance within DMC error bar



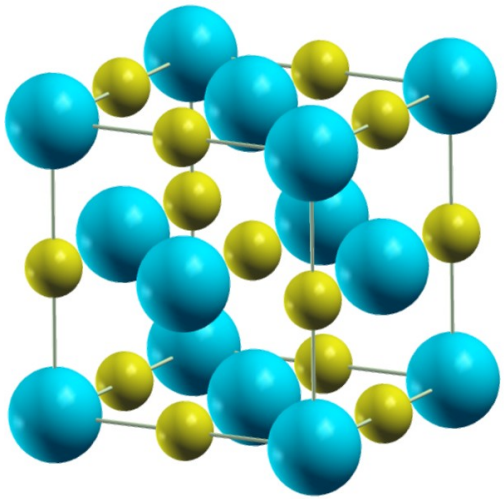
S. Grimme (2012)

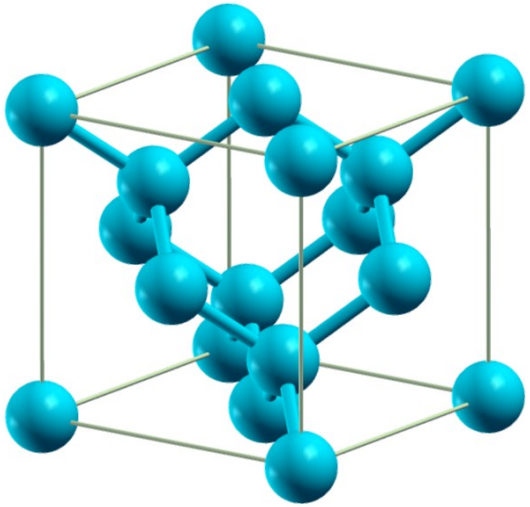
MAE of PBE+MBD vs. DMC:
1.6 kcal/mol

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

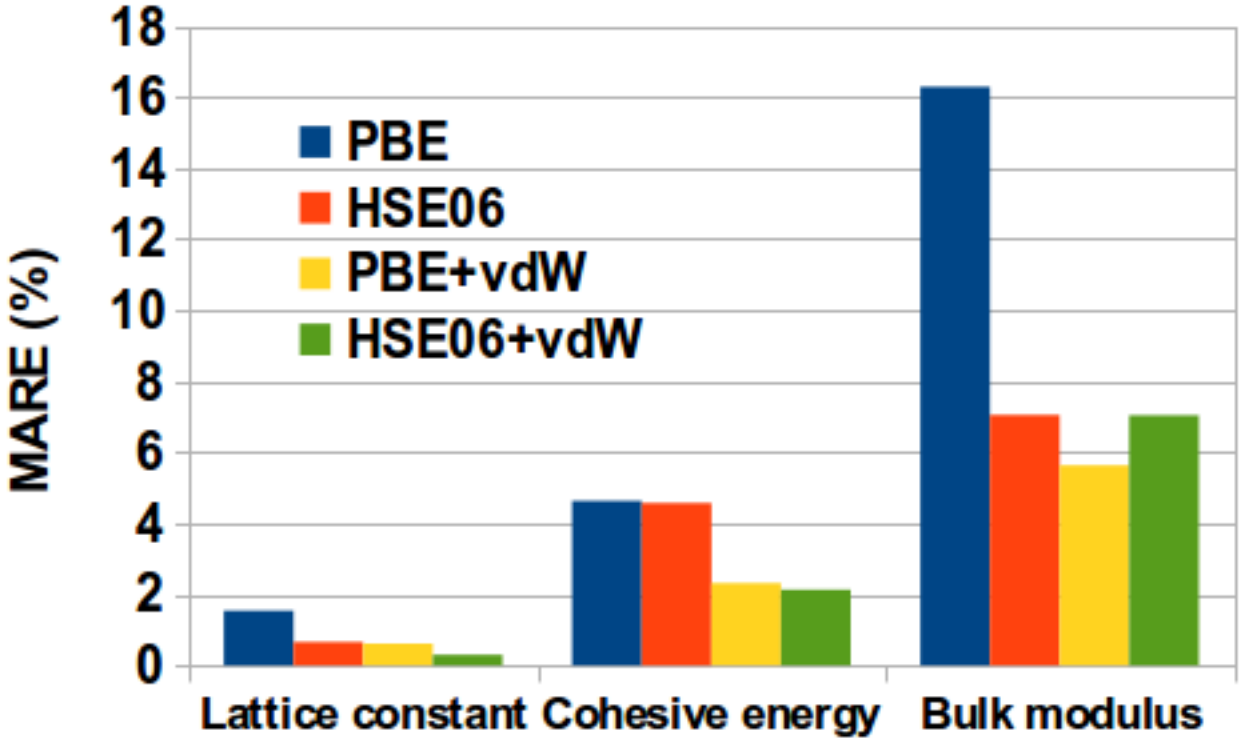


Van der Waals Interactions in Hard Solids





Semiconductors and ionic solids

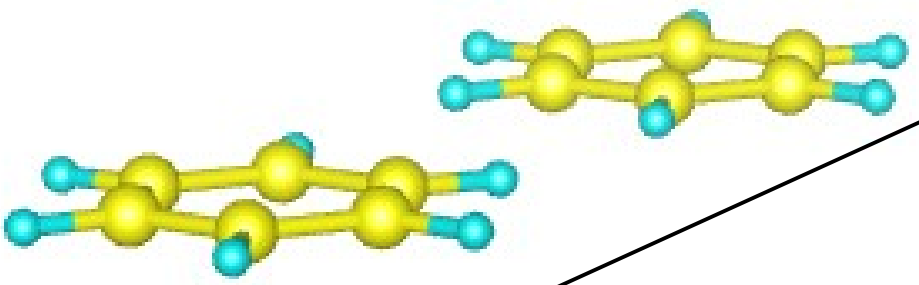


The vdW energy contributes 0.2-0.3 eV/atom to the cohesive energy, 3-17 GPa to the bulk modulus, and 0.01-0.15 A to the lattice constant

G.-X. Zhang, A. Tkatchenko, J. Paier, H. Appel, M. Scheffler, ***Phys. Rev. Lett.*** (2011).

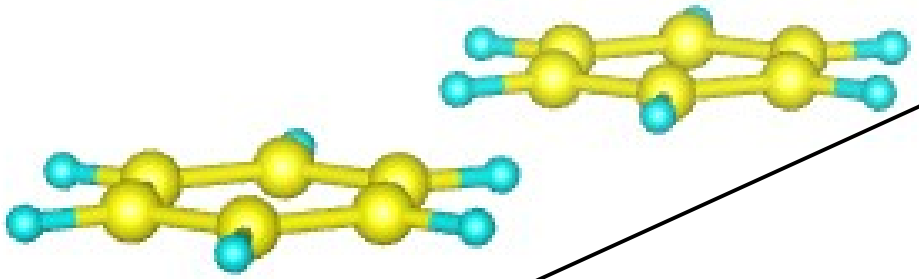
Summary

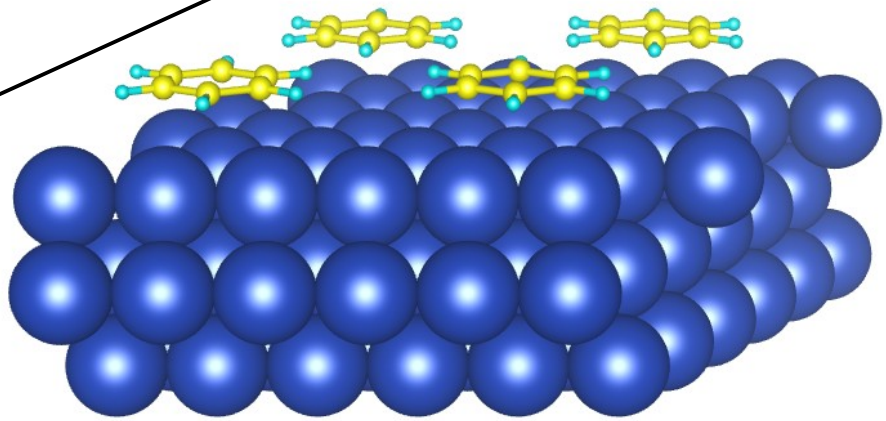
$$C_{6,\mathrm{eff}}^{ii} = C_{6,\mathrm{eff}}^{ii}[n(\mathbf{r})]$$

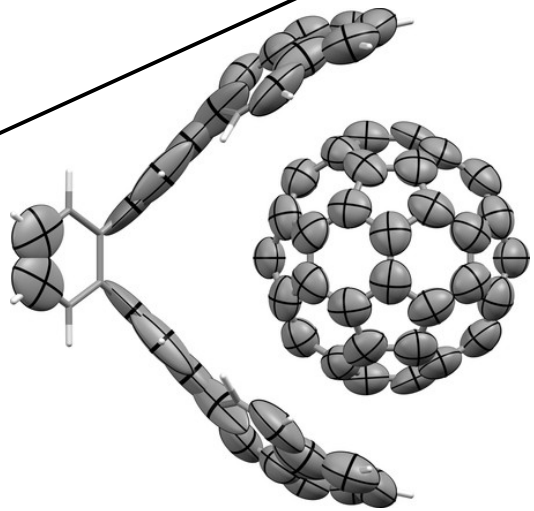


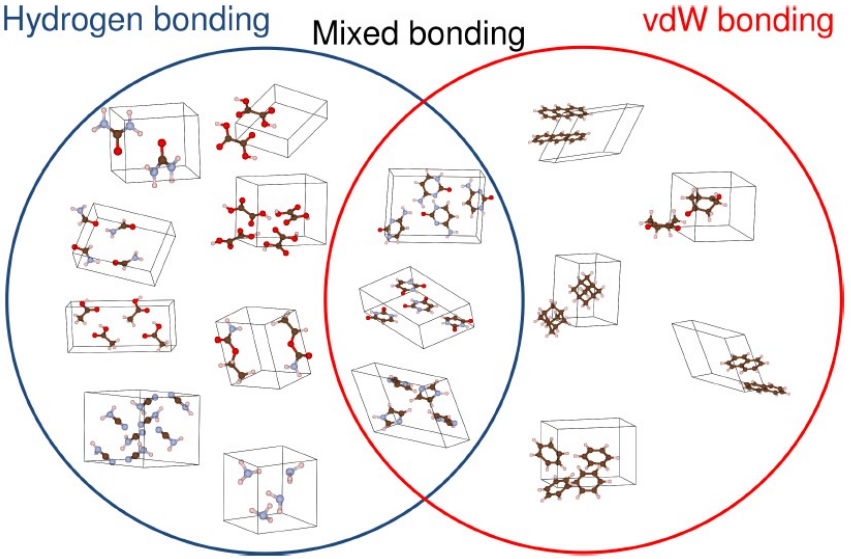
Summary

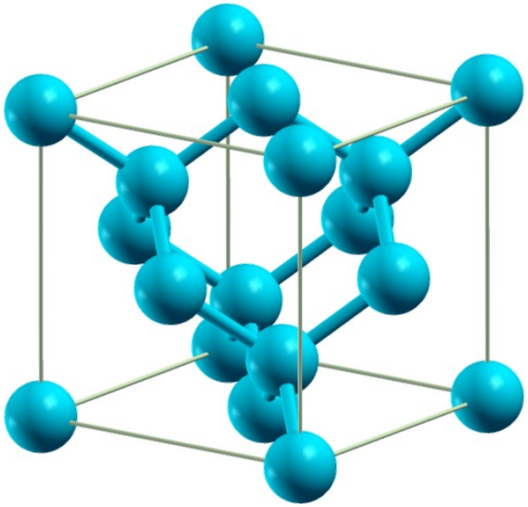
$$C_{6,\mathrm{eff}}^{ii} = C_{6,\mathrm{eff}}^{ii}[n(\mathbf{r})]$$







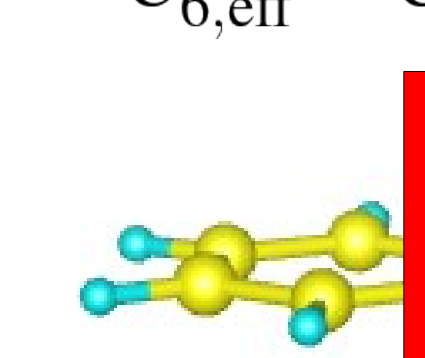


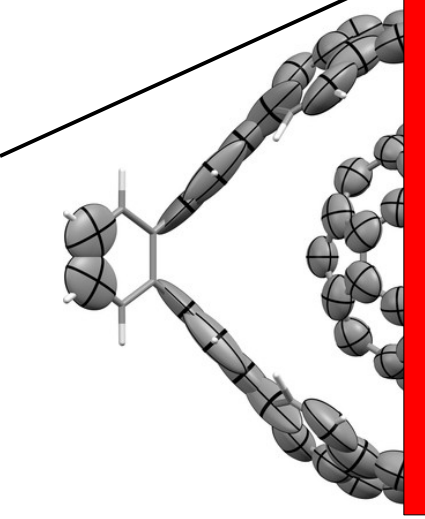


$$E_c = -\int_0^\infty \frac{d\omega}{2\pi} \int_0^1 d\lambda \mathrm{Tr}\left((\chi_\lambda(\mathbf{r_1}, \mathbf{r_2}; i\omega) - \chi_0(\mathbf{r_1}, \mathbf{r_2}; i\omega)) \frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} \right)$$

Summary

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





Van der Waals interactions arise due to collective fluctuations of the electron density (they are part of long-range electron correlation)

Now, it is possible to compute the many-body vdW energy accurately and efficiently for complex (non-metallic) materials

… Perhaps it is time to move beyond rather simplified empirical pairwise models ...

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