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First-Principles Approaches to van der Waals Interactions: Conceptual Understanding and Practical Methods

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UNIVERSITÉ DU
LUXEMBOURG

Hands-on DFT and Beyond

Barcelona, Aug 28, 2019

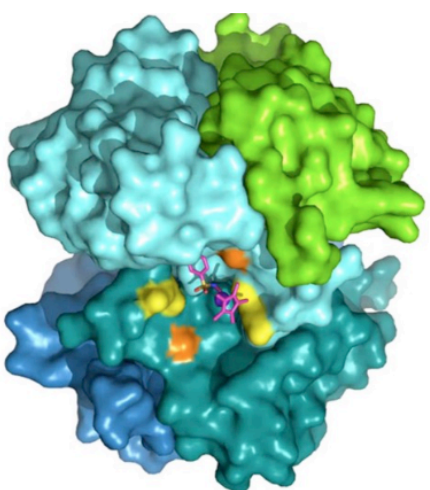


BERLIN BIG
DATA CENTER

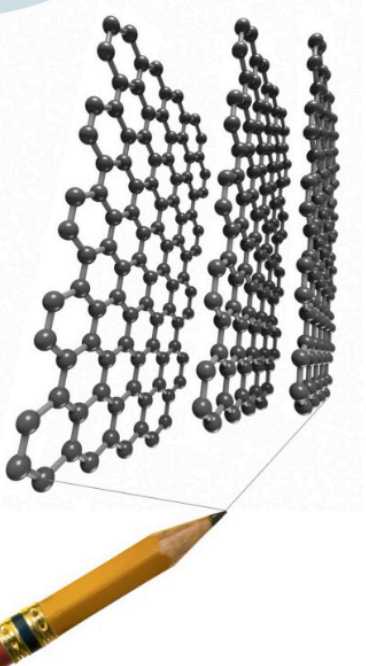
$$\hat{H}\Psi = E\Psi$$



Gecko



Proteins



Graphite sheets

Van der Waals interactions



Water

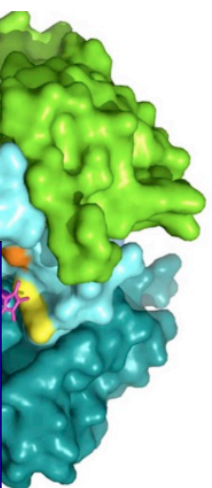


Polymers

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



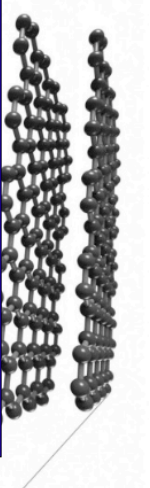
Gecko



Prote

“Chemistry of the 20th century was about intramolecular interactions; chemistry of the 21st century will be about intermolecular interactions.”

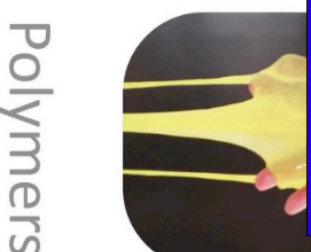
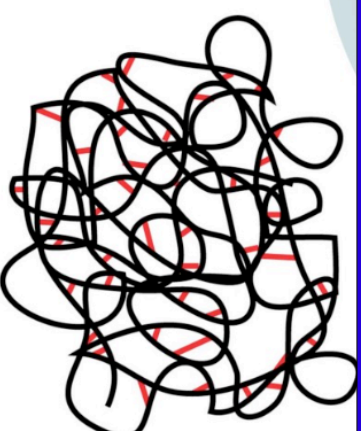
Mark Ratner, 2004



neets

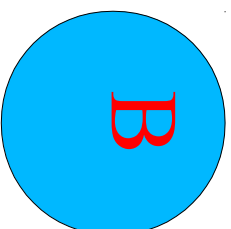
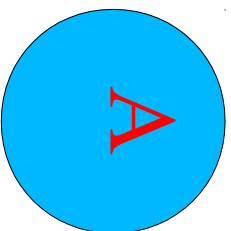


Water

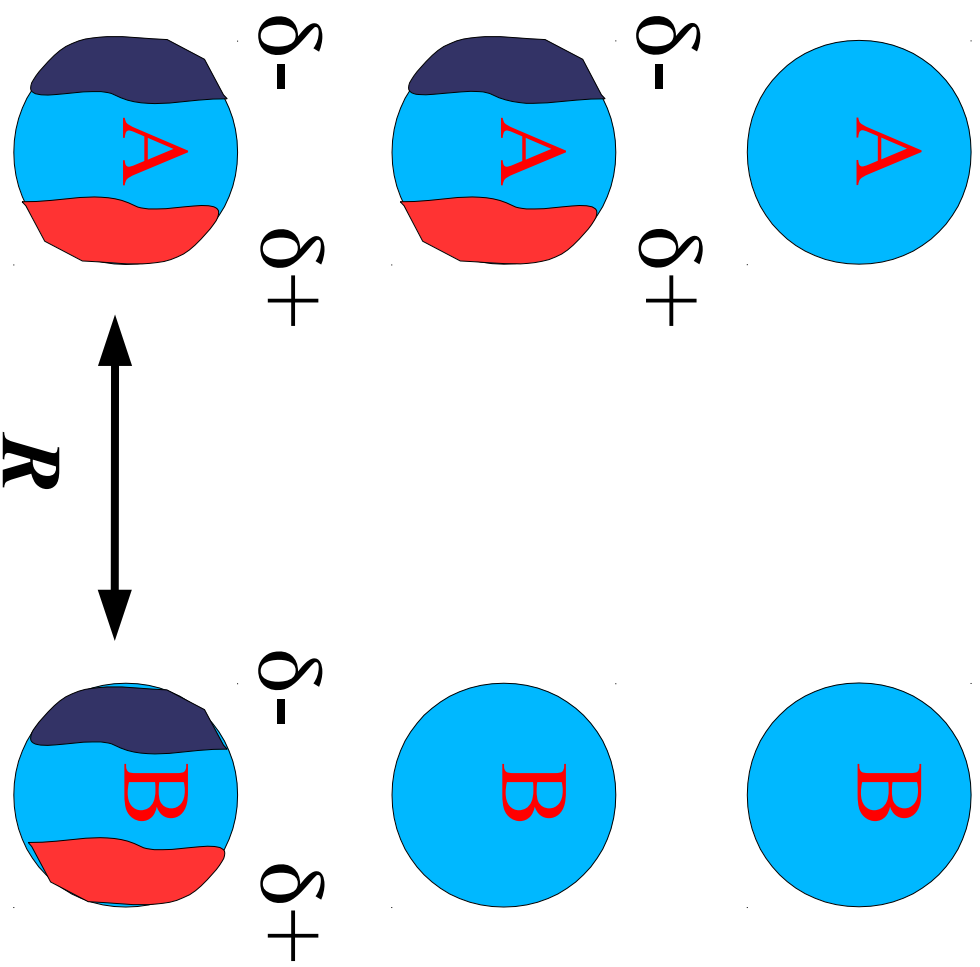


Polymers

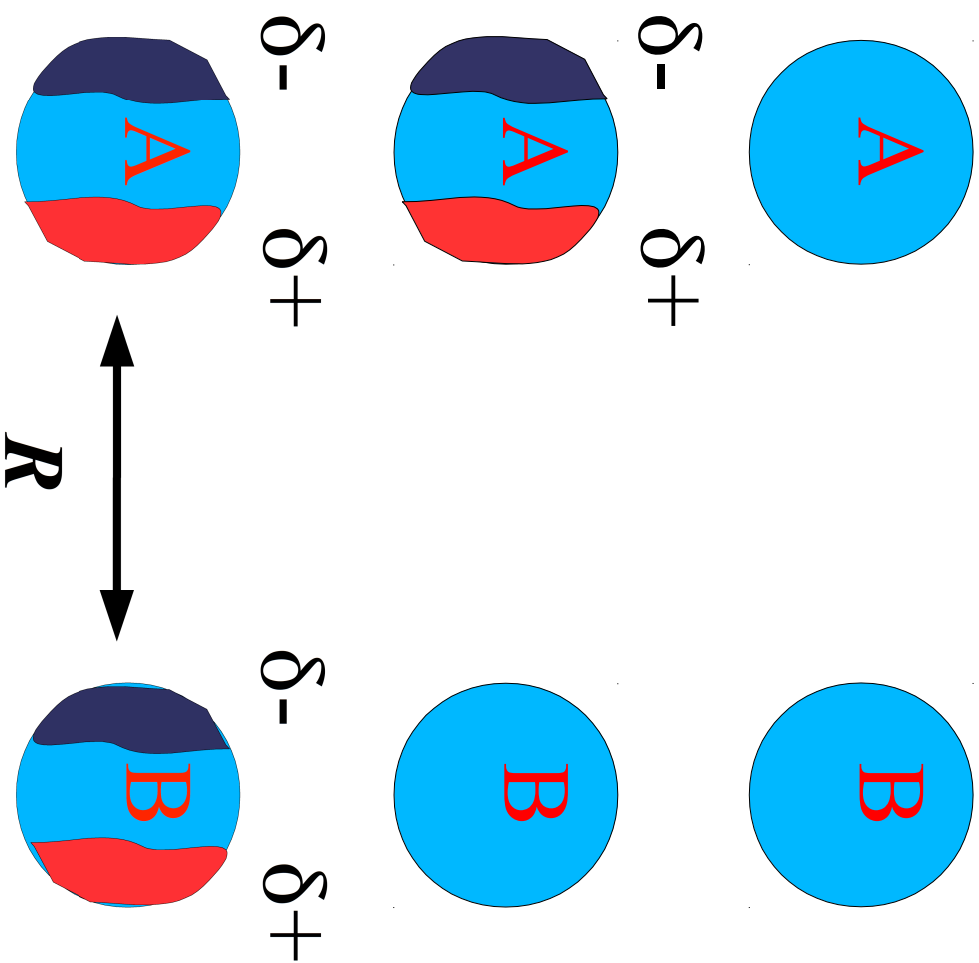
Textbook picture of vdW interactions



Textbook picture of vdW interactions

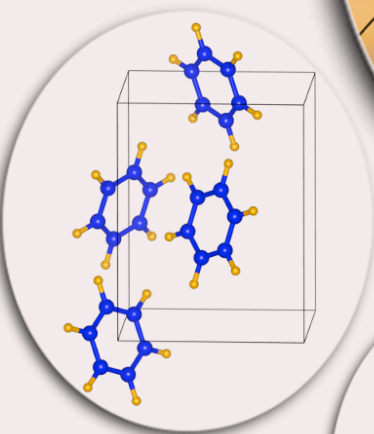
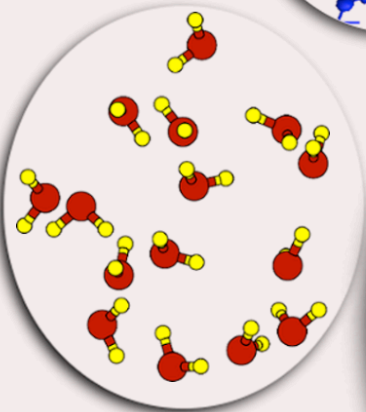
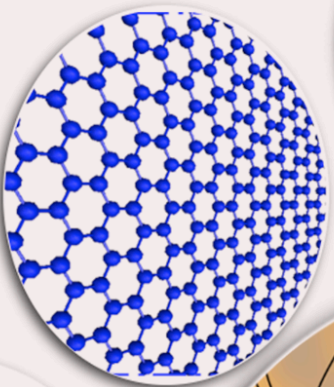
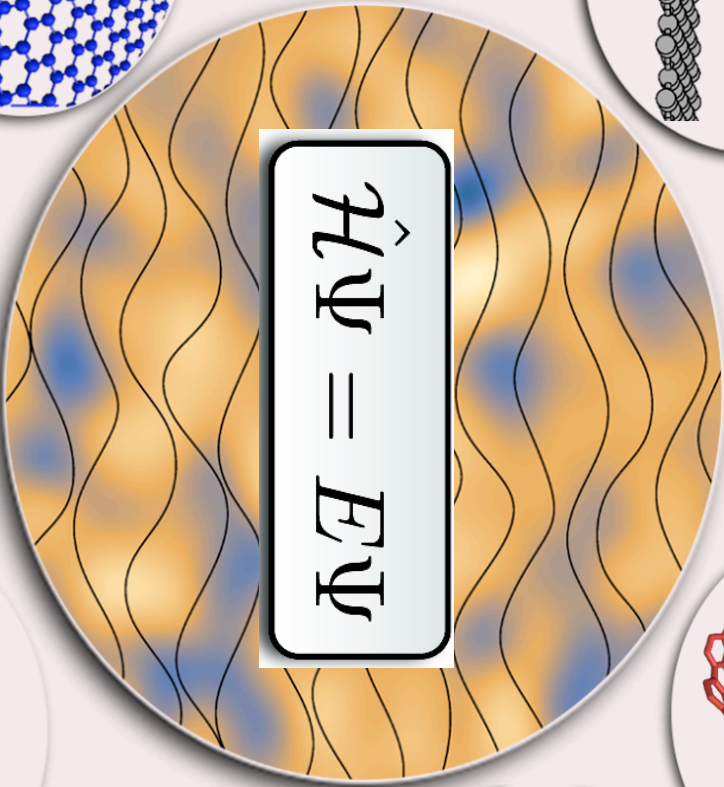
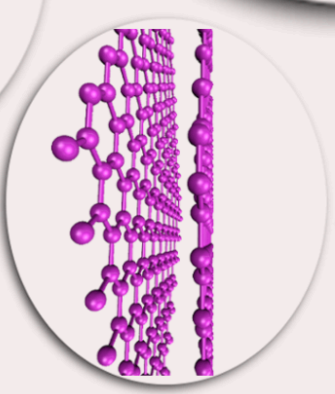
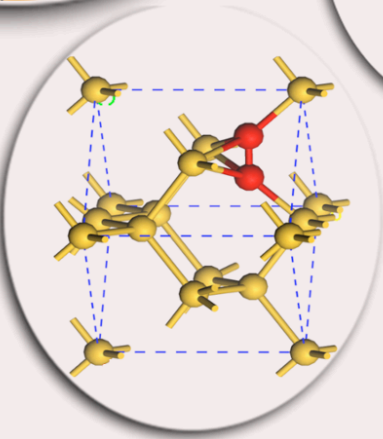
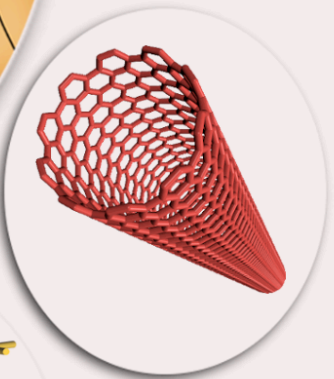
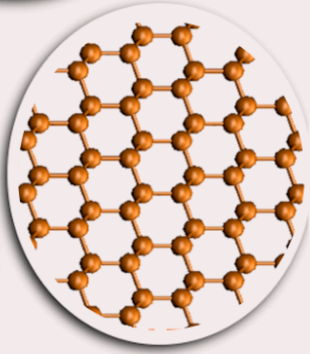
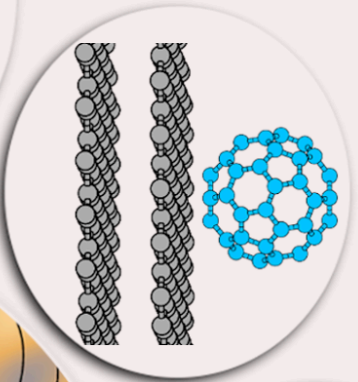


Textbook picture of vdW interactions



$$E_{\text{vdW}}^{(2)} = -\frac{C_6^{\text{AB}}}{R_{\text{AB}}^6}$$

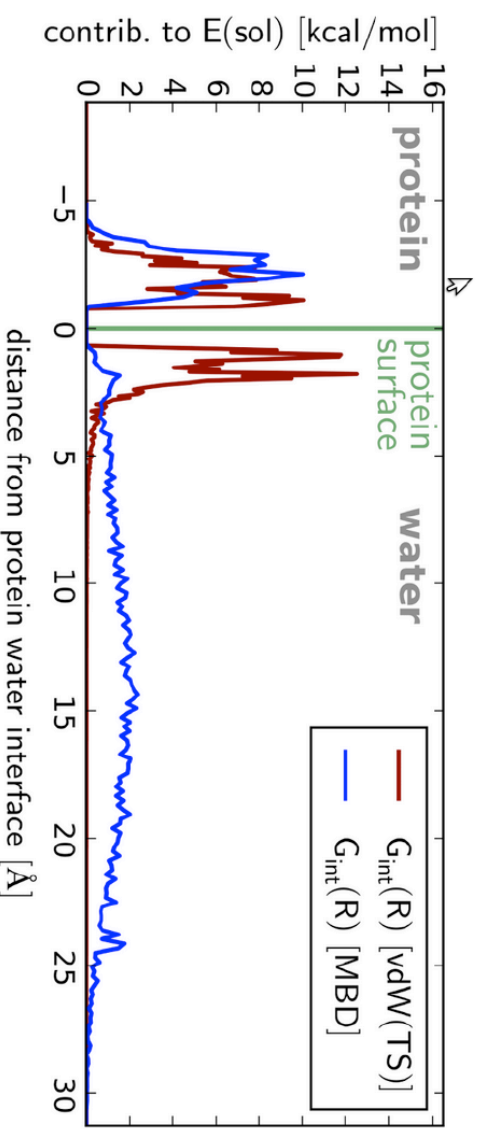
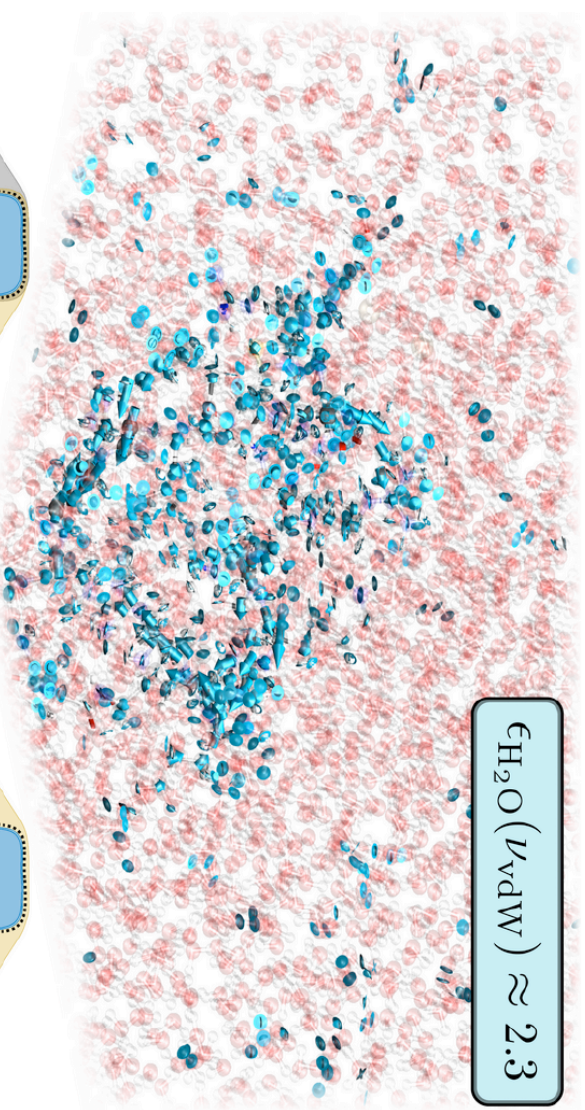
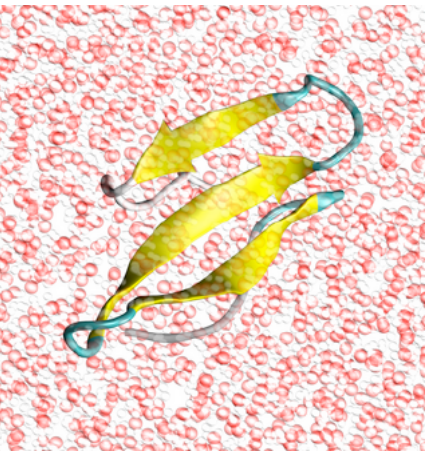
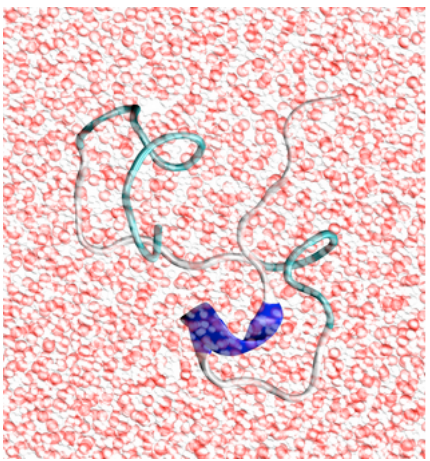
$$\rightarrow C_6^{\text{AB}} = \frac{3}{\pi} \int \alpha_A(i\omega) \alpha_B(i\omega) d\omega$$



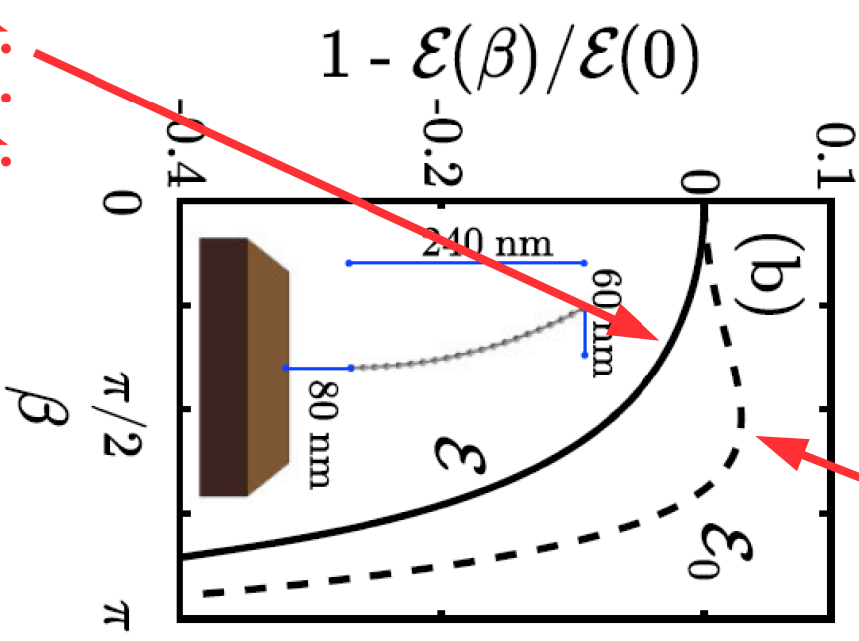
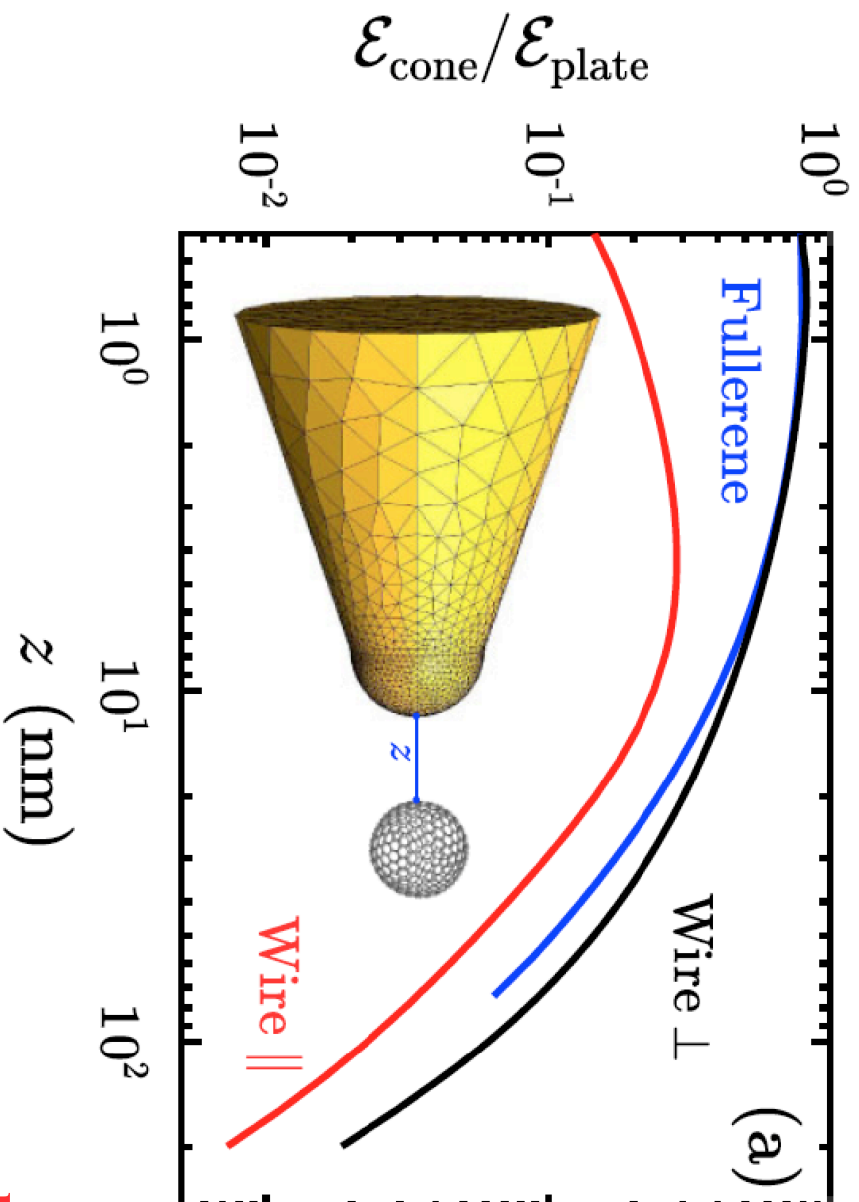
Science 351, 1171 (2016); *Chem. Rev.* 117, 4714 (2017).

There is plenty of room ... at the top

Nanoscale: van der Waals Interactions in Biology



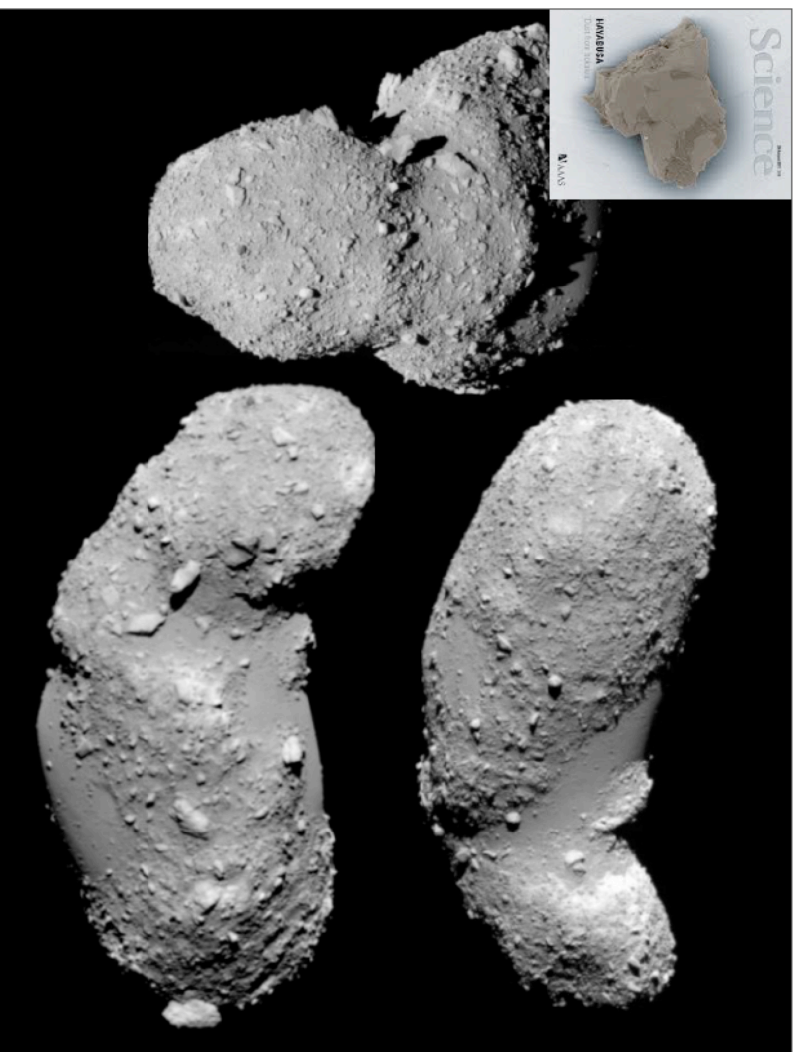
Mesoscale: Relativity, Quantum Effects, and Thermal Phonons Matter



P. S. Venkataram, J. Hermann, A. Tkatchenko, and A. W. Rodriguez,
Phys. Rev. Lett. 118, 266802 (2017); *Science Adv.*, in print (2019).

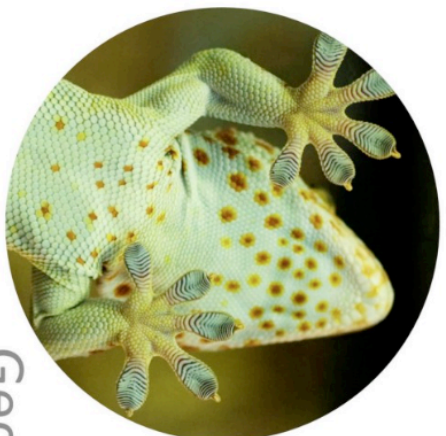
Macroscale: There is Plenty of Room at the Top

QM effects at macroscopic scales:

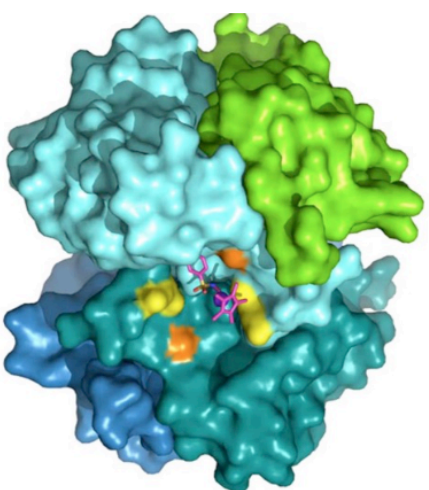


B. Rozitis *et al.*, *Nature* 512, 174 (2014).

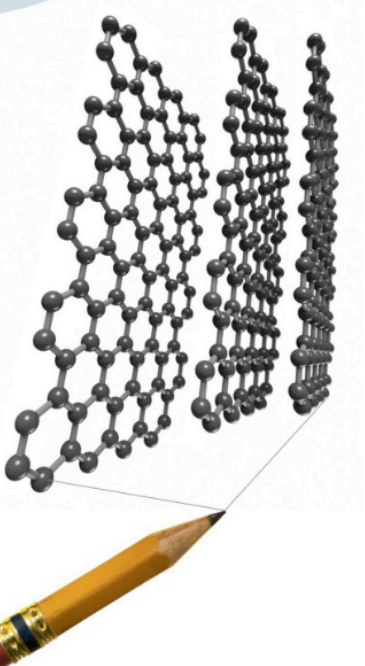
$$\hat{H}\Psi = E\Psi$$



Gecko



Proteins

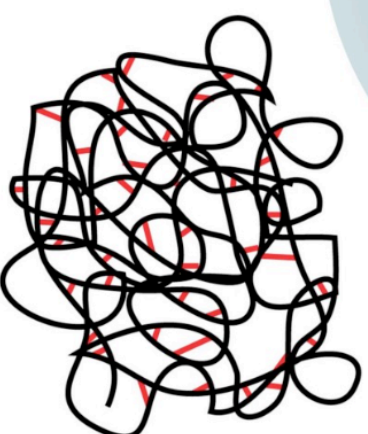


Graphite sheets

Van der Waals interactions



Water

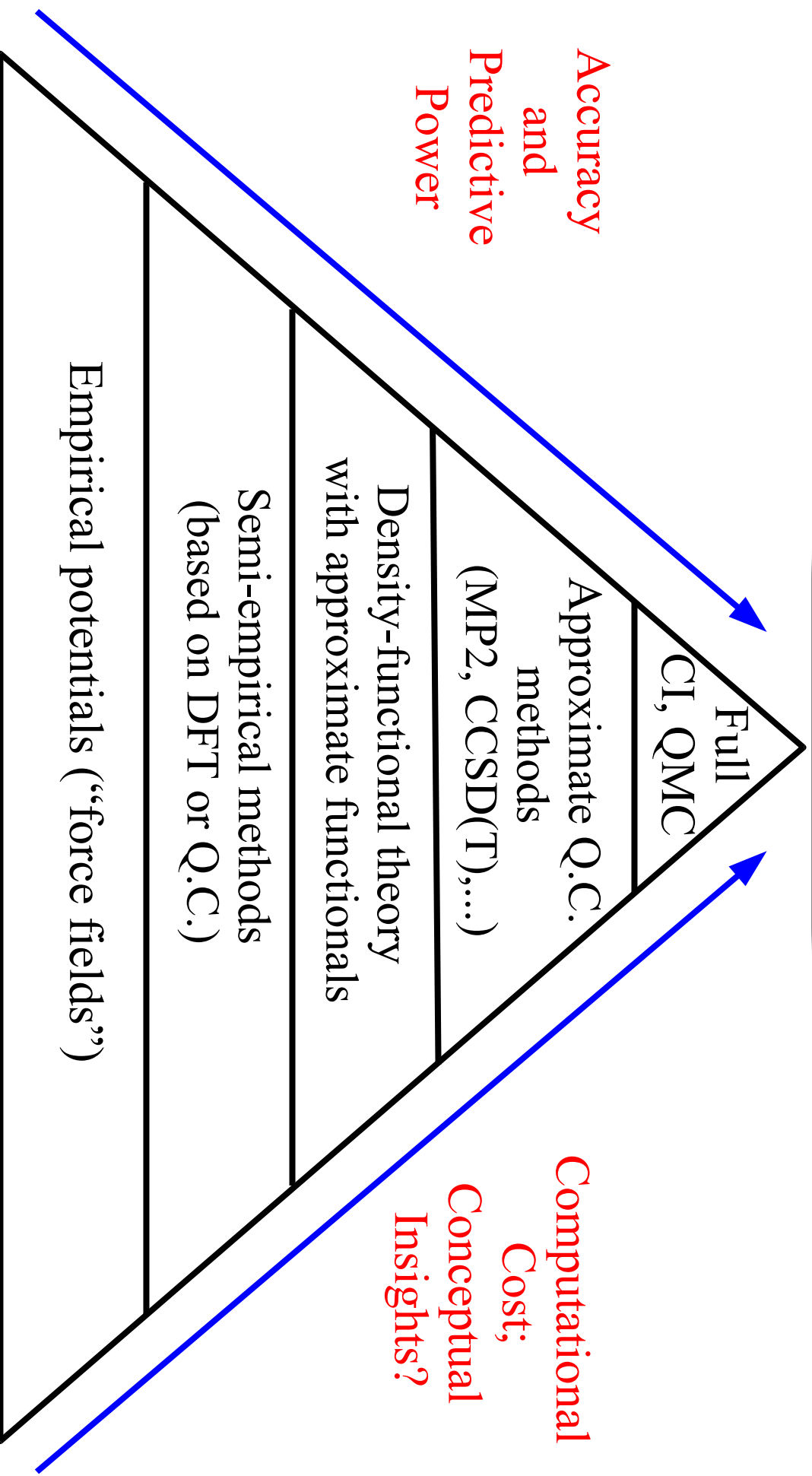


Polymers



Current state of the art of atomistic modeling

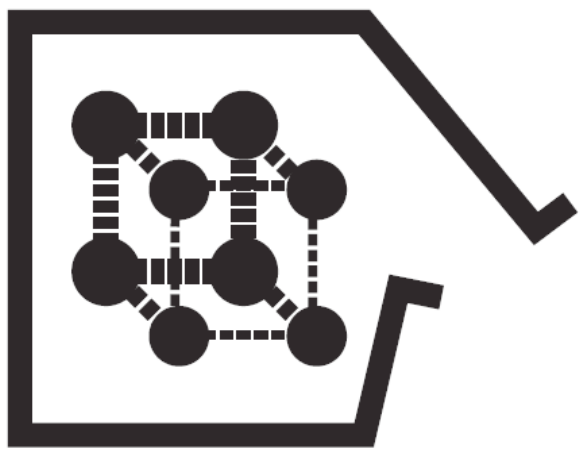
$$\hat{H}\Psi = E\Psi$$



Density-functional approximations (DFA): *Solid starting point*

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

Exchange and Correlation
functionals



LDA **PBE**
 $n(\vec{r}); \vec{\nabla} n(\vec{r});$

$\nabla^2 n(\vec{r}); \dots$
TPSS, SCAN

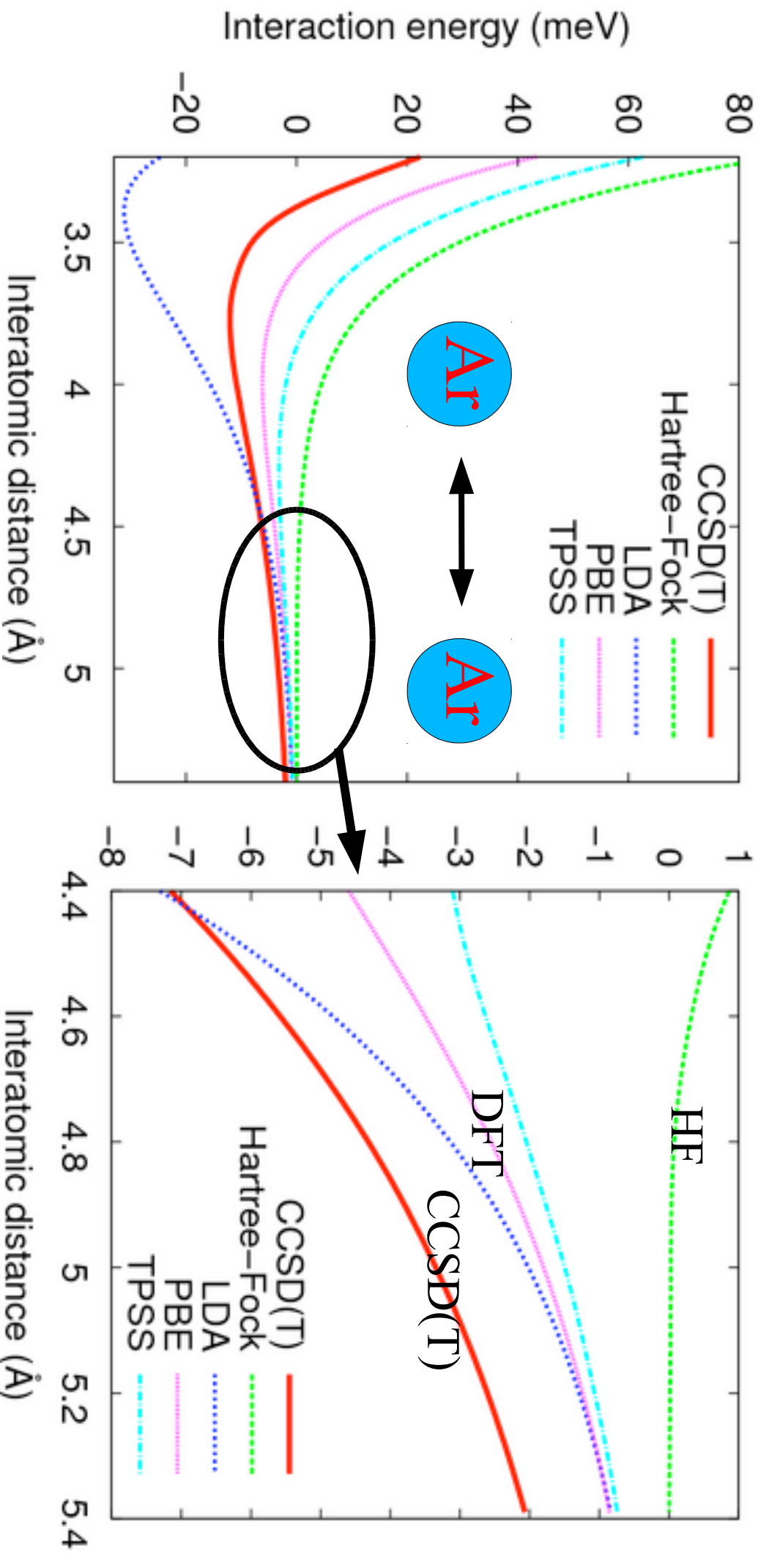


- X Self-interaction error**
- X Lack of long-range correlation (van der Waals interactions)**

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

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

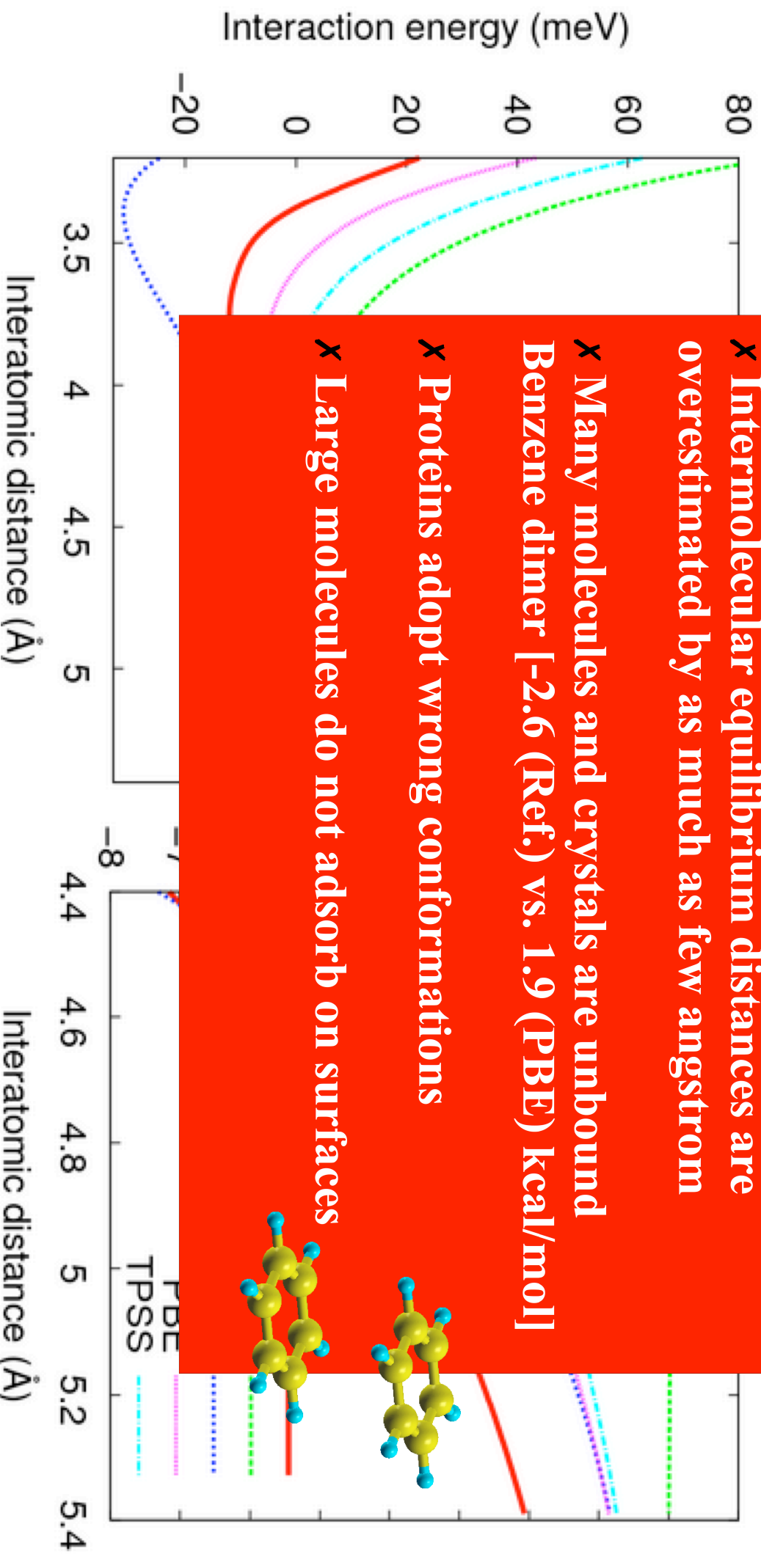
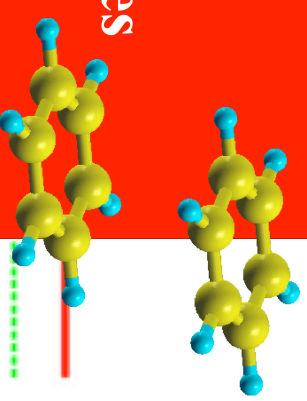
$$E^{disp}(R) = - \left(f_6(R) \frac{C_6}{R_6} + f_8(R) \frac{C_8}{R_8} + f_{10}(R) \frac{C_{10}}{R_{10}} + \dots \right)$$



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

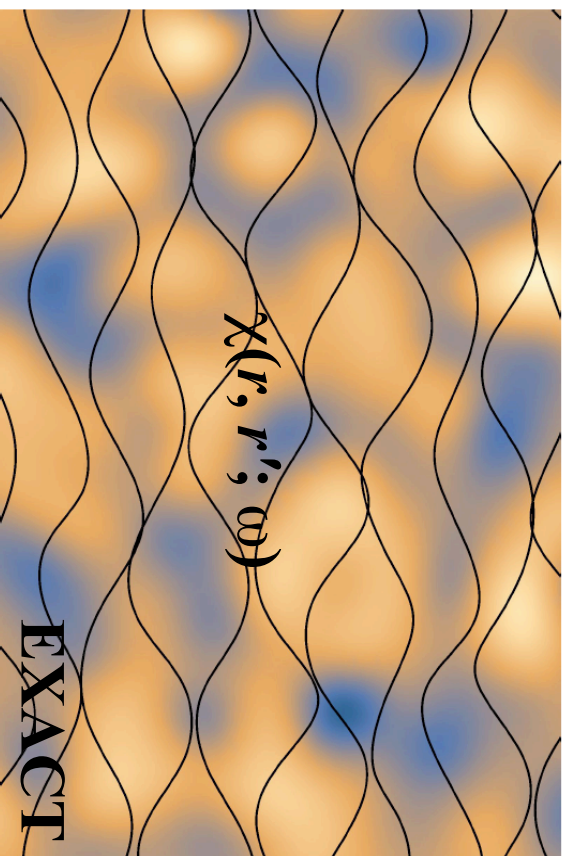
$$E^{disp}(R) = - \left(f_6(R) \frac{C_6}{R_6} + f_8(R) \frac{C_8}{R_8} + f_{10}(R) \frac{C_{10}}{R_{10}} + \dots \right)$$

- ✗ 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



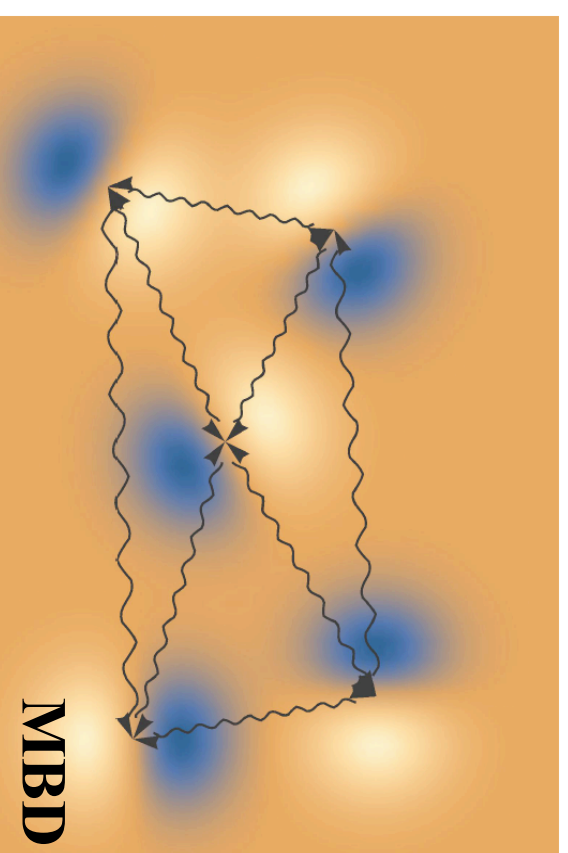
a

$$-\frac{1}{2\pi} \int_0^\infty du \text{Tr} [(x_{\hat{\lambda}} - x_0)v]$$



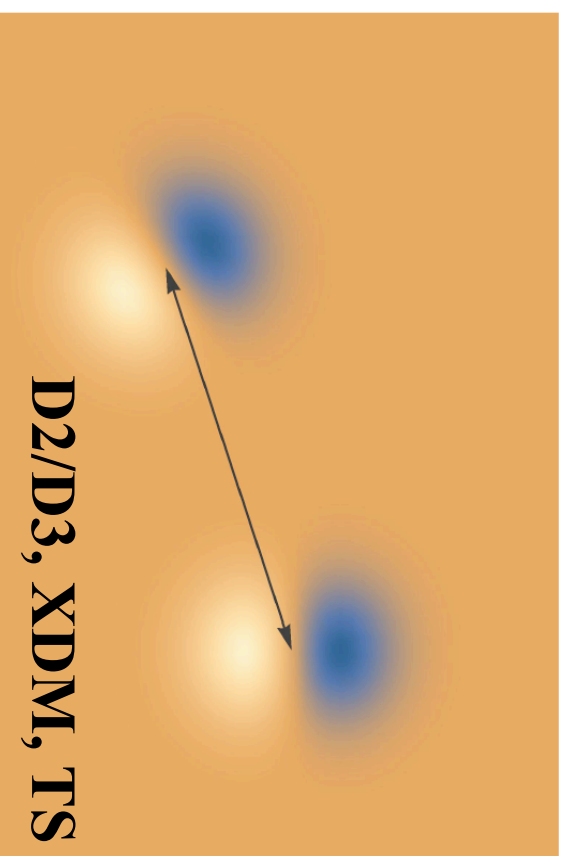
b

$$-\frac{1}{2\pi} \int_0^\infty du \sum_{n=2}^{\infty} \frac{1}{n} \text{Tr} [(\alpha_m \tilde{\mathbf{T}})^n]$$



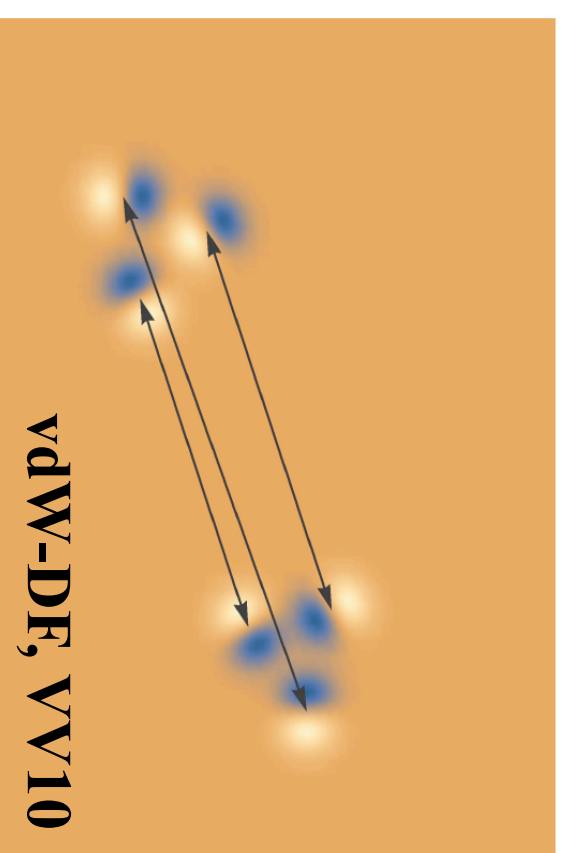
c

$$-\frac{1}{2} \sum_{ij} C_{6,ij} f(R) R^{-6}$$



d

$$-\frac{1}{2} \iint dr dr' n(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$



(Approximate) vdW-inclusive DFT methods

Reviews:

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

*J. Hermann, R. A. DiStasio Jr., and A. Tkatchenko, **Chem. Rev.** 117, 4714 (2017).*

*M. Stöhr, T. Van Voorhis, and A. Tkatchenko, **Chem. Soc. Rev.** 48, 4118 (2019).*

Concepts and methods for dispersion in DFT

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

Concepts and methods for dispersion in DFT

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

- 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.*); “non-empirical” SCAN (*Perdew 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); Perdew et al. PRL (2015); and many others ...

Langreth-Lundqvist functional
(vdW-DF-04 and vdW-DF-10,
and VV10, opt-vdW-DF, ...)

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

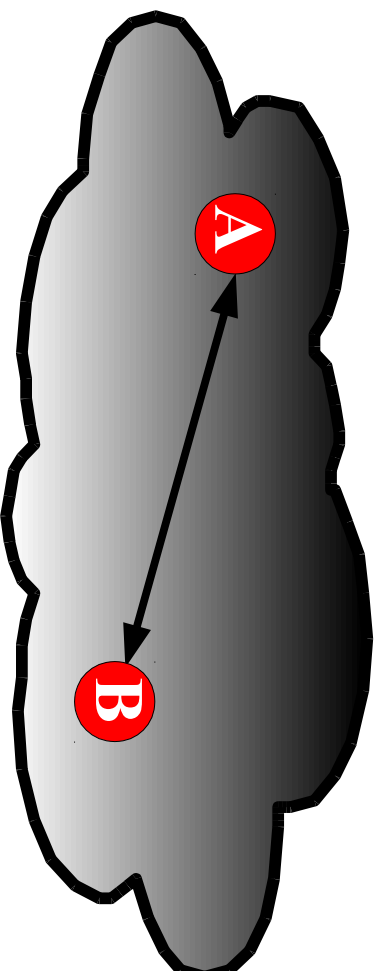
vdW-DF-10

- Exchange: revPBE
- Exchange: PW86
- Local corr.: LDA
- Local corr.: LDA
- No free parameters
- 2 parameters
- C_6 error: $\sim 20\%$
- C_6 error: $\sim 40\%$ (*)

(*) *Hydrov 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 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

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

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

- 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**.

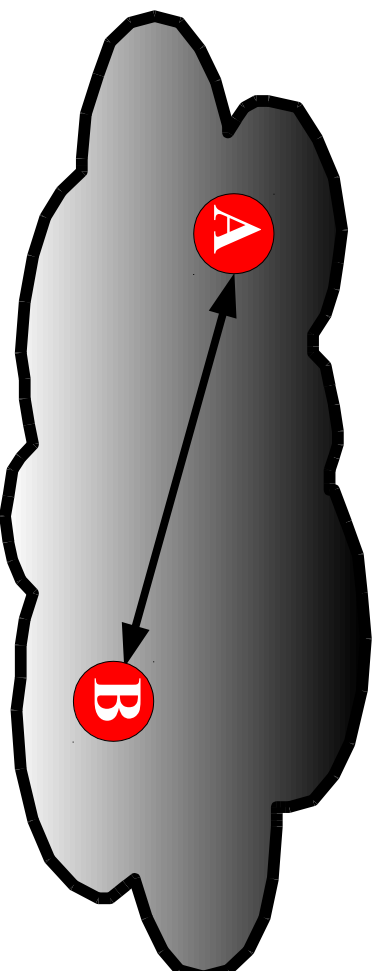
Evolution of interatomic vdW methods

- Grimme's D1,D2,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 $\sim 20\%$ - 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 ?

$$E^{vdW}(R) = - \left(f_6(R) \frac{C_6'}{R_6} + f_8(R) \frac{C_8'}{R_8} + f_{10}(R) \frac{C_{10}'}{R_{10}} + \dots \right)$$

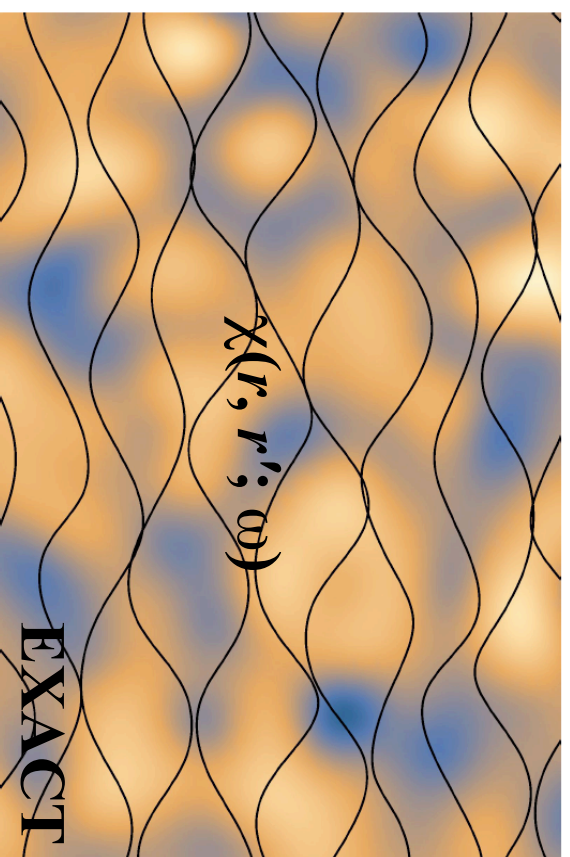


- 1) Long-range electrodynamic response for fluctuating dipoles
- 2) Non-additive many-body vdW energy beyond two-body

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

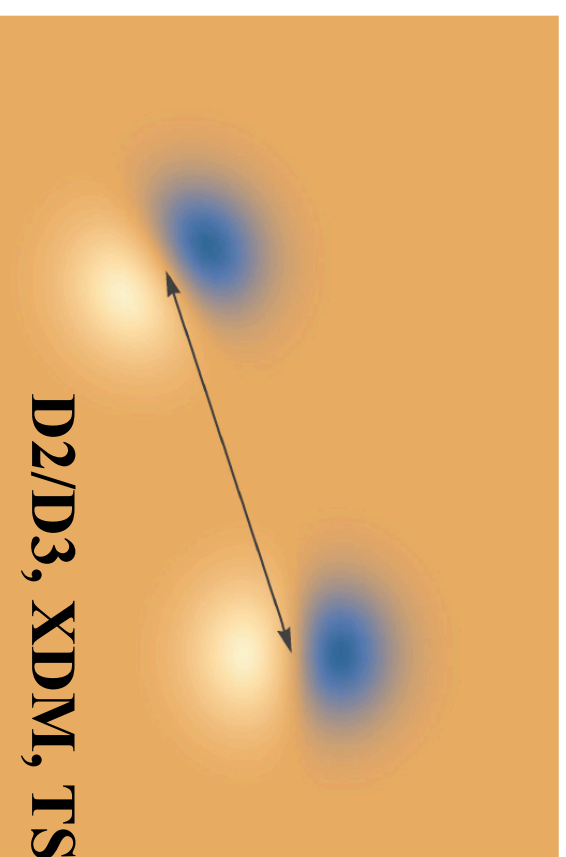
a

$$-\frac{1}{2\pi} \int_0^\infty du \text{Tr} [(x_{\hat{\lambda}} - x_0)v]$$



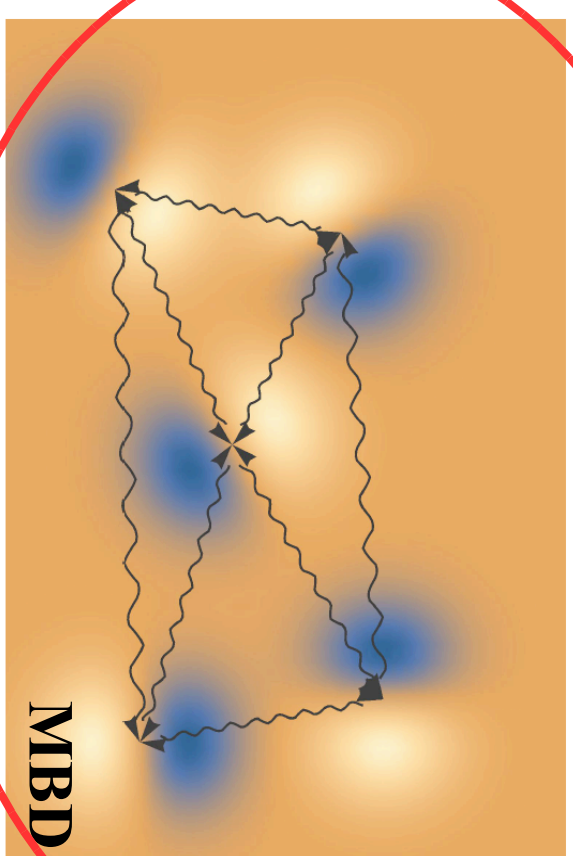
c

$$-\frac{1}{2} \sum_{ij} C_{6,ij} f(R) R^{-6}$$



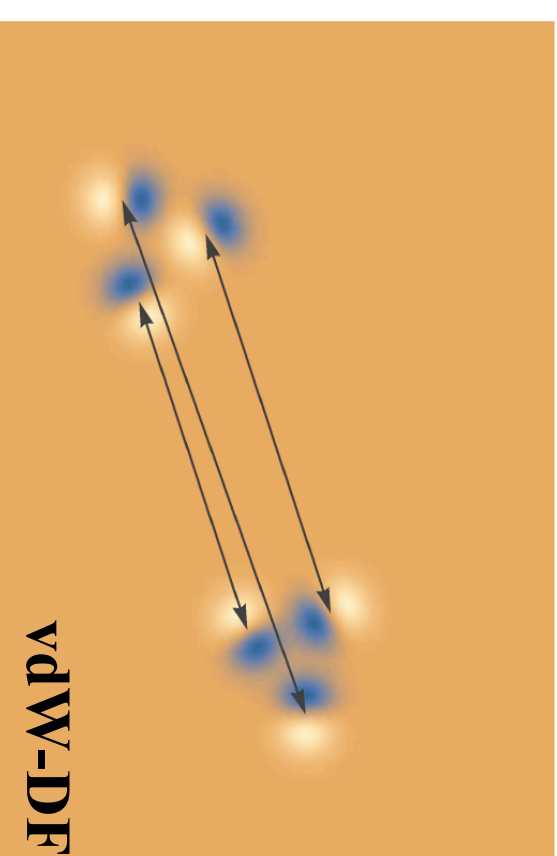
b

$$-\frac{1}{2\pi} \int_0^\infty du \sum_{n=2}^\infty \frac{1}{n} \text{Tr} [(\alpha_n \hat{\mathbf{T}})^n]$$



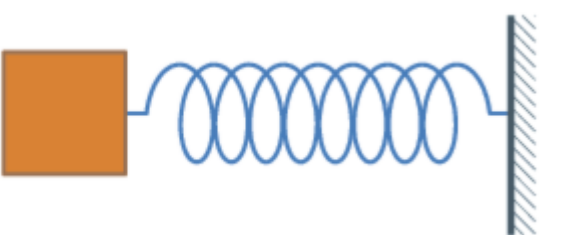
d

$$-\frac{1}{2} \iint^{\infty} dr dr' n(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$



Chem. Rev. 117, 4714 (2017); *Rev. Mod. Phys.* 88, 045003 (2016).

Physicist's Dream: Mapping Electrons to Quantum Harmonic Oscillators (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*; *F. Manby*; ...

Physicist's Dream: Mapping Electrons to Quantum Harmonic Oscillators (QHO)

Nucleus (\mathbf{q})

$$\hat{H}_0 = \frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m} + \frac{1}{2} m \omega^2 (\mathbf{r} - \mathbf{R})^2$$

Harmonic bond (ω)

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Model proposed by *W. L. Bade* (1957); and used by *B. J. Berne*,
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Harmonic bond (ω)

$$\begin{aligned} \hat{H} = & \sum_{k=1}^N \hat{H}_{0k} + \frac{1}{2} \sum_{k \neq k'=1}^N q_k q_{k'} \left(\frac{1}{|\mathbf{R}_k - \mathbf{R}_{k'}|} \right. \\ & \left. + \frac{1}{|\mathbf{r}_k - \mathbf{r}_{k'}|} - \frac{1}{|\mathbf{r}_k - \mathbf{R}_{k'}|} - \frac{1}{|\mathbf{R}_k - \mathbf{r}_{k'}|} \right) \end{aligned}$$

“Electron” ($-\mathbf{q}, m$)

Model proposed by *W. L. Bade* (1957); and used by *B. J. Berne*,
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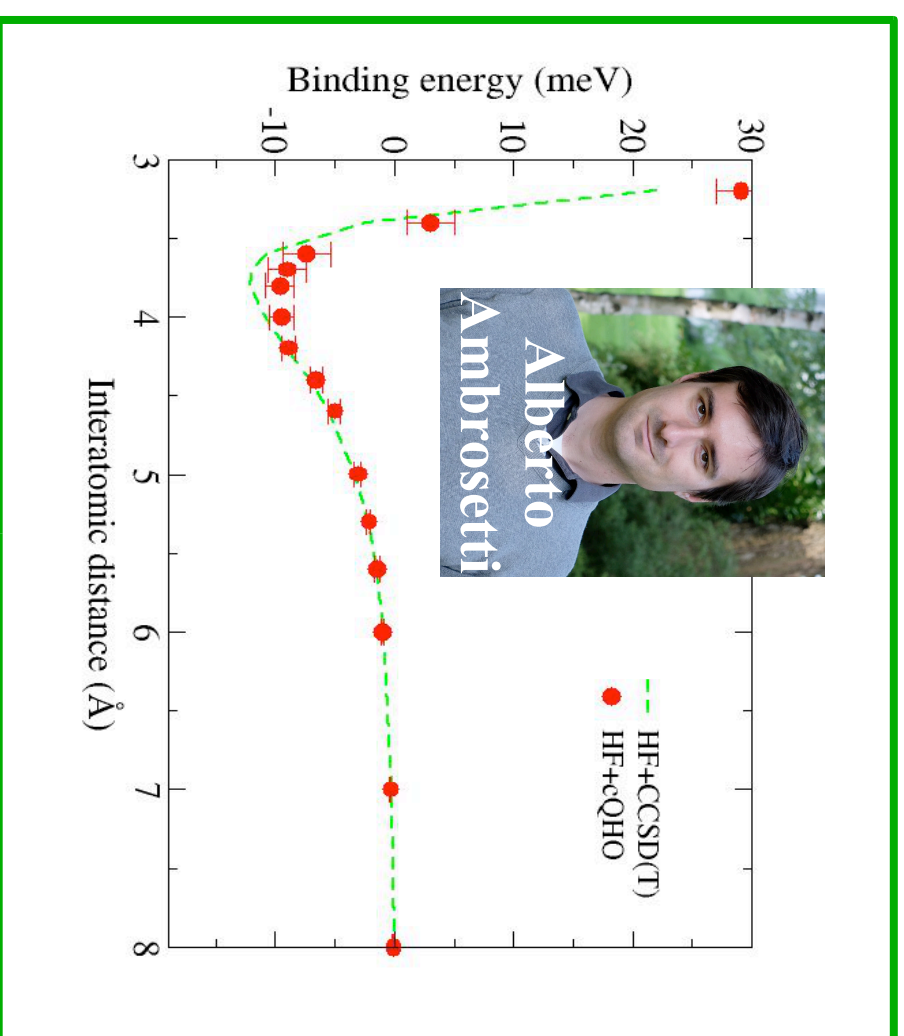
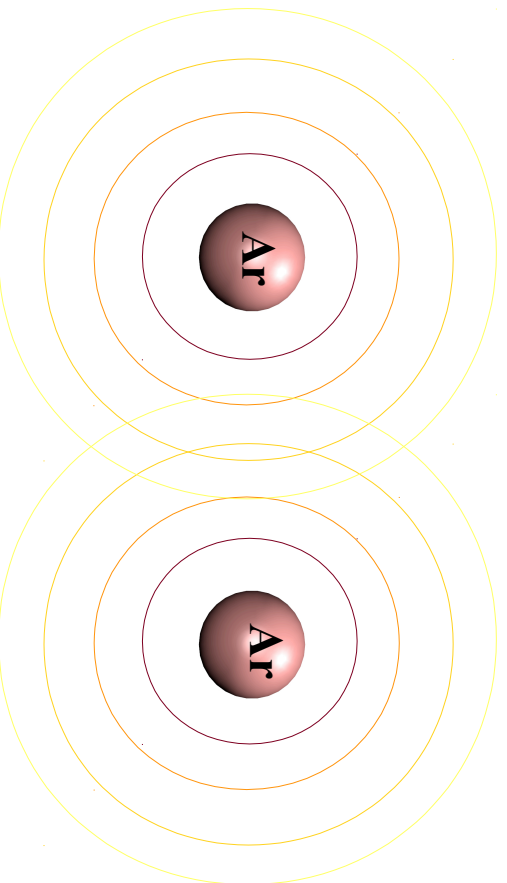
From Dream to Reality:

Argon dimer described accurately by two oscillators

- Coupled QHO correlation energy computed through **Diffusion Monte Carlo** (exact for bosons)

$$\{\alpha(0), C_6, C_8\} \rightarrow \{m, q, \omega\}$$

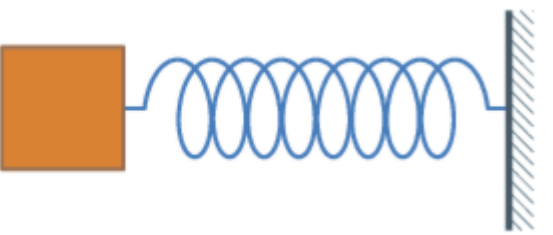
- Exchange and electrostatic energy from **Hartree-Fock** (HF)



HF+cQHO: almost exact binding energy curve (within 3 meV at minimum) without any specific adjustments.

Fermionic effects in correlation energy kick in only at very short distances.

Efficient model for valence excitations: Quantum Harmonic Oscillator (QHO) in the dipole approximation



Nucleus (q)

Harmonic bond (ω)

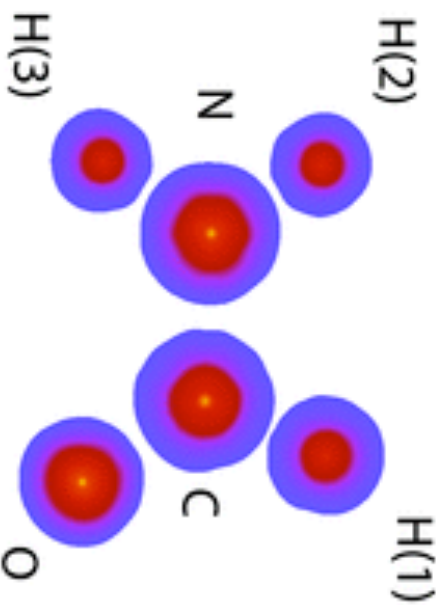
“Electron” ($-q, m$)

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

$$H = -\frac{1}{2} \sum_{p=1}^N \nabla_{\mu_p}^2 + \frac{1}{2} \sum_{p=1}^N \omega_p^2 \mu_p^2 + \sum_{p>q}^N \omega_p \omega_q \sqrt{\alpha_p^0 \alpha_q^0} \mu_p \mathcal{T}_{pq} \mu_q$$

Quantum Harmonic Oscillators in Molecules and Solids from First Principles

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



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

α^0 and ω^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)

Modeling Real Materials: DFT+MBD Method

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

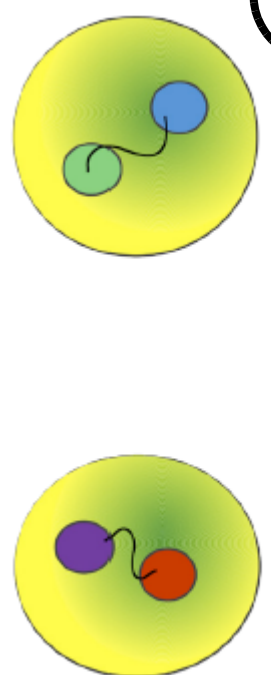
1

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


Valence electrons
projected to oscillators
(Tkatchenko-Scheffler)

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

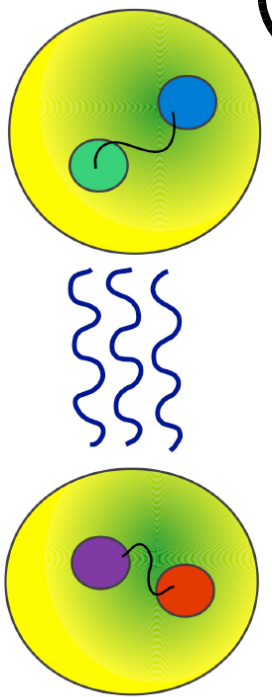
2

$$\tilde{\alpha} = \alpha - \alpha T <_R \tilde{\alpha}$$


Dyson-like
short-range
electrodynamical
screening

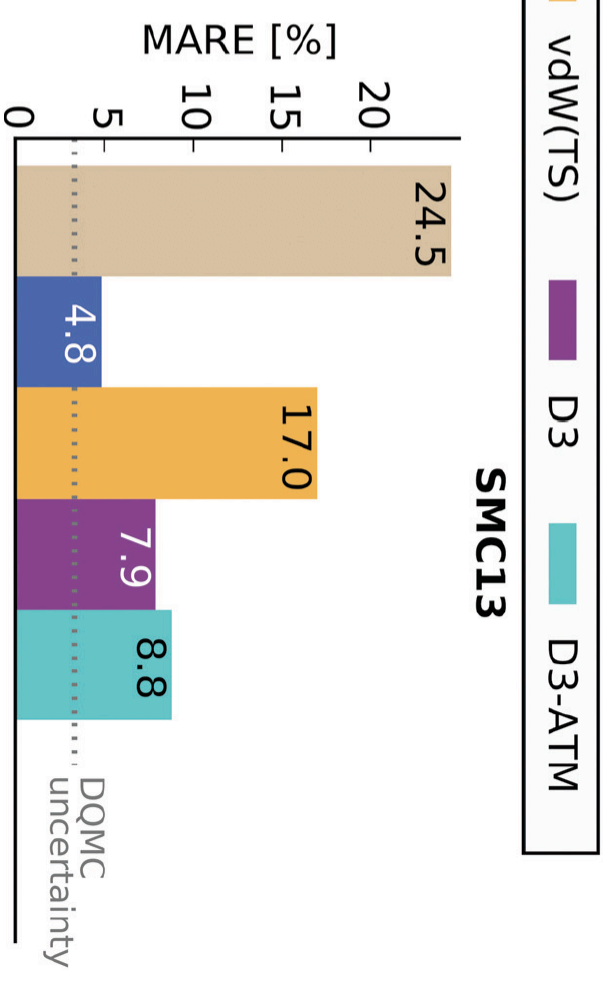
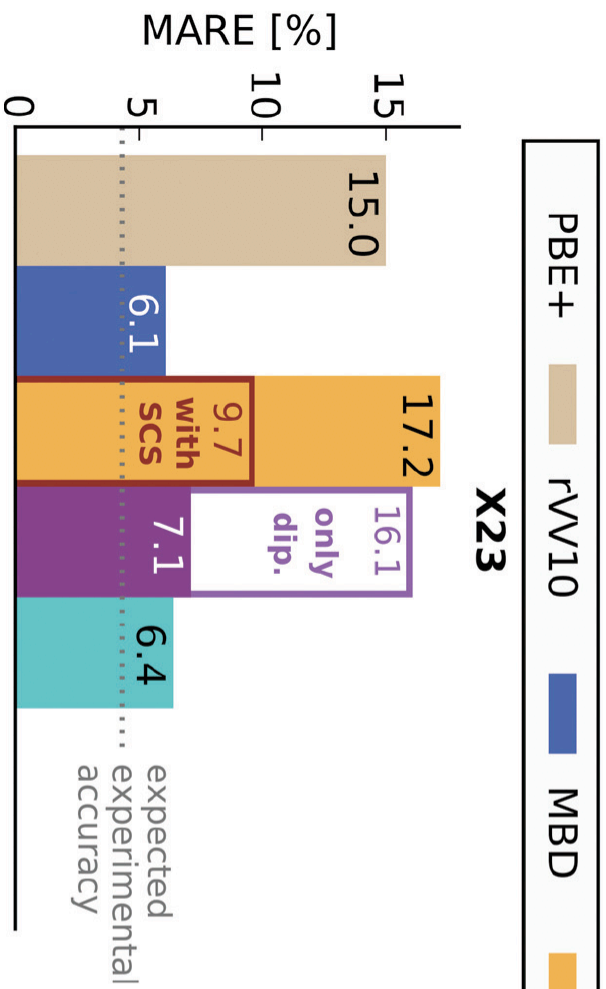
A. Ambrosetti,
R. A. DiStasio Jr.,
A. M. Reilly,
A. Tkatchenko,
J. Chem. Phys. (2014)

3

$$\hat{H} >_R \Psi = E \Psi$$


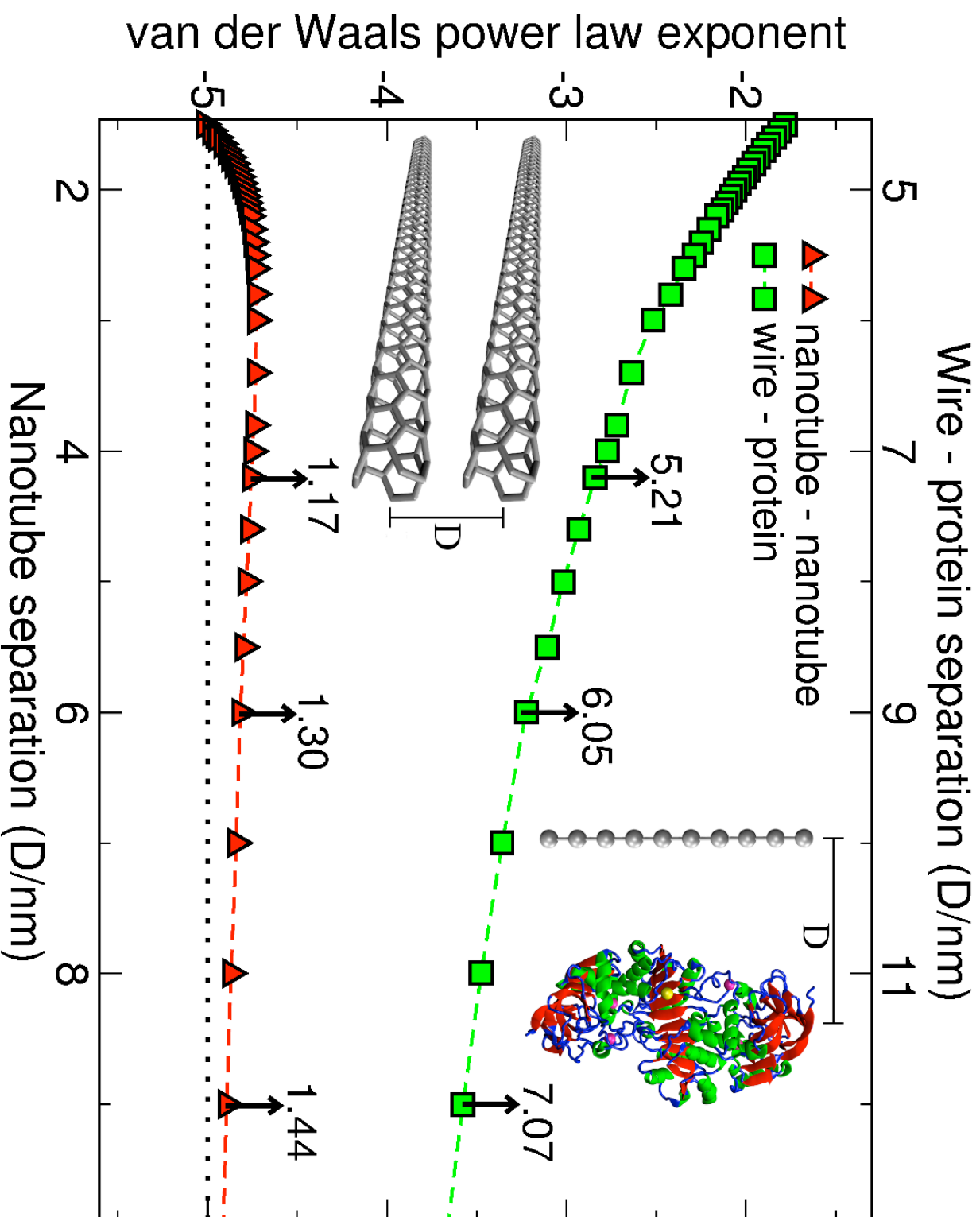
Long-range
correlation
energy
calculated
using SE

Modeling Real Materials: Method Benchmark

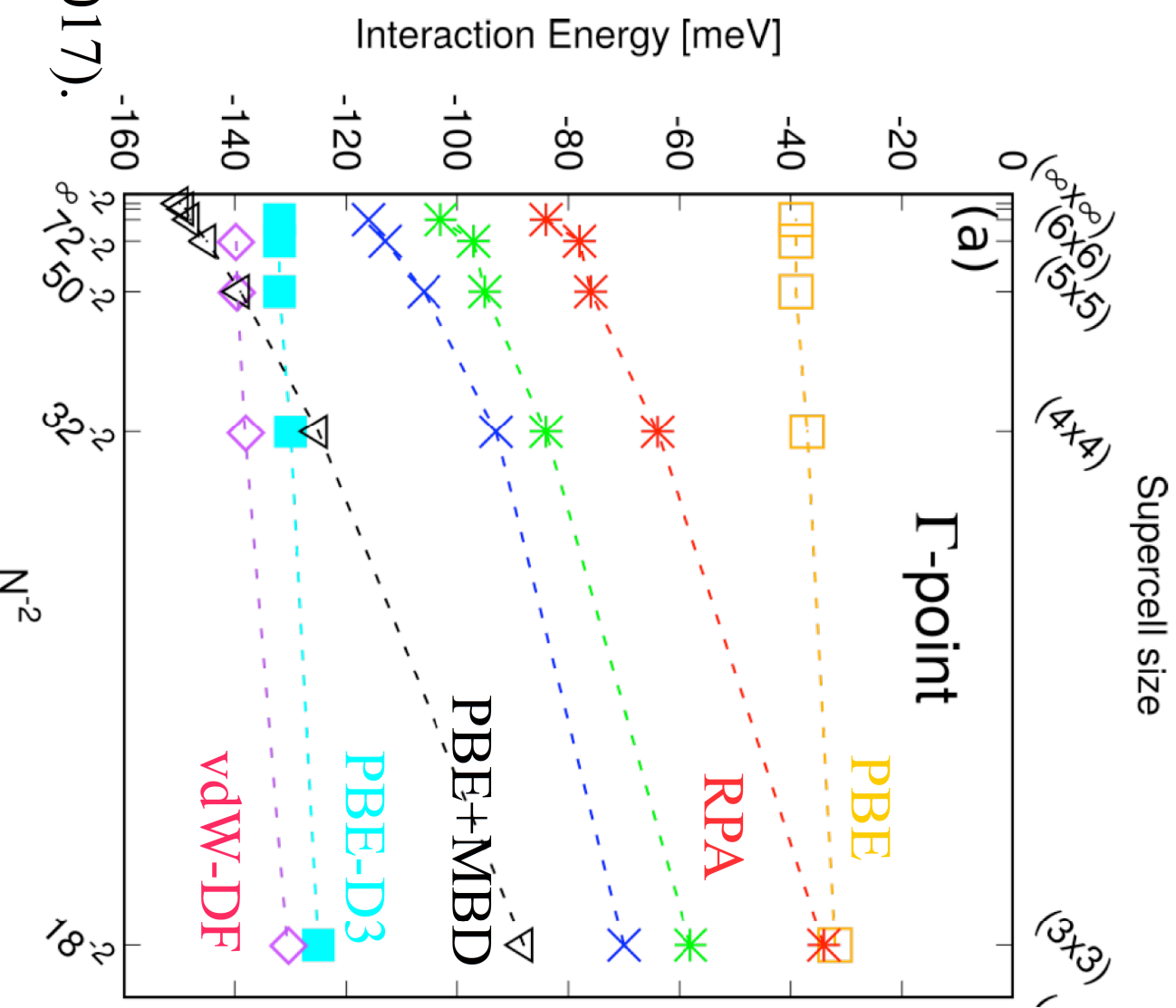
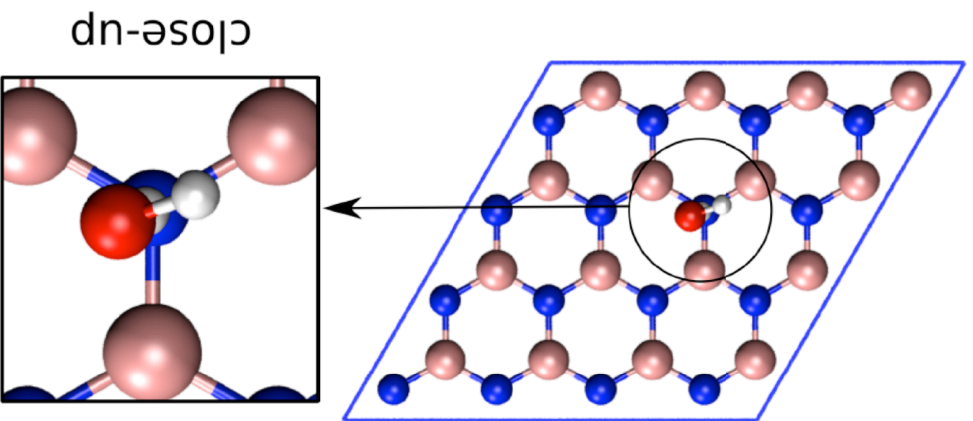


M. Stöhr, T. Van Voorhis, and A. Tkatchenko, Chem. Soc. Rev.
48, 4118 (2019).

Quantum fluctuations and van der Waals interactions in Nano/Bio-materials



Quantum fluctuations and van der Waals interactions in Nano/Bio-materials



Y. Al-Hamdani *et al.*,
J. Chem. Phys. 147, 044710 (2017).

Repulsive under confinement
PRL 118, 210402 (2017)

Highly non-additive

*Couple strongly to phonons,
leading to “vdW entropy”*

PRL 114, 176802 (2015)

*Can have visible effect on
electronic properties*

*Very long range
(20-30 nm at nanoscale;
 μm or longer at
mesoscale)*



**Van der Waals
interactions**

PRL 118, 266802 (2017)

*Retardation
(finite speed of light)
can be important*

Nature Comm. 9, 3017 (2018)

*In presence of charges
vdW couples to electric fields*

*Decay as a complex
sum over R^{-n} terms*

Chem. Rev. 117, 4714 (2017); *Rev. Mod. Phys.* 88, 045003 (2016).