Tutorial 3:
van der Waals Interactions

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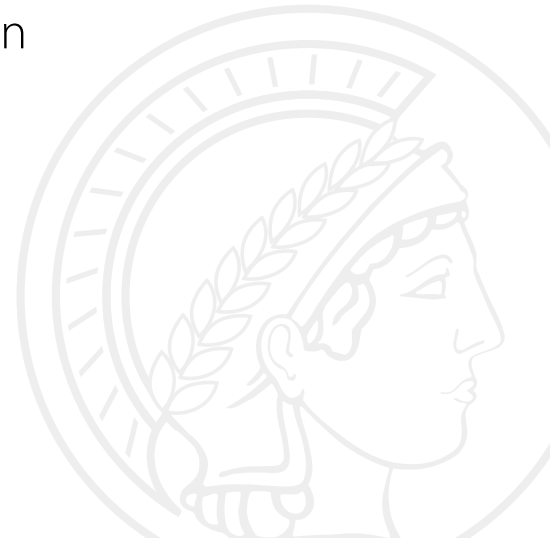


Pairwise approaches to van der Waals

Interatomic methods

$$\sum_{i<j} f(R_{ij}) \frac{C_{6,ij}[n]}{R_{ij}^6}$$

- Grimme's DFT-D*n*[1]
- Tkatchenko–Scheffler[2]
  C_6 functionals of density
+ Fast, simple
– Atomic parameters input
– Problems with metals and charge-transfer character

Non-local functionals

$$\iint n(\boldsymbol{r}_1)\Phi[n](\boldsymbol{r}_1, \boldsymbol{r}_2)n(\boldsymbol{r}_2)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2$$

- Langreth–Lundqvist[3]
- Vydrov–van Voorhis[4]
+ Pure density functionals
– Questionable for molecules, metals

[1]Grimme, J. Comp. Chem. (2004) [2]Tkatchenko, Scheffler, Phys. Rev. Lett. (2009)
[3]Dion, Phys. Rev. Lett. (2004) [4]Vydrov, van Voorhis, Phys. Rev. Lett (2004)

How to go beyond pairwise van der Waals

- Random-phase approximation (RPA) framework

$$E_c = -\frac{1}{2\pi}\int_0^\infty \mathrm{d}\omega \sum_{n=2}^{\infty} \frac{1}{n} \mathrm{Tr}[(\chi_0 V)^n]$$

Many-body dispersion[1]

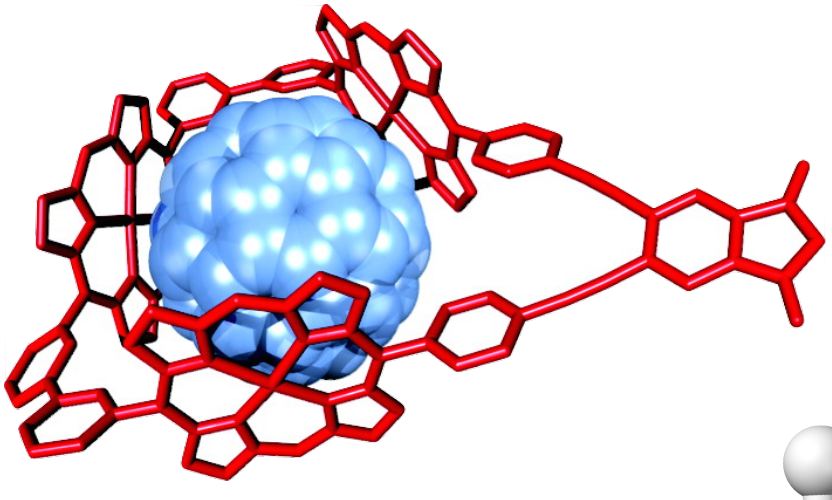
- χ_0 from localized atomic response functions
- Based on dipole harmonic oscillators
\+ Can be solved analytically
– Open problem with metals

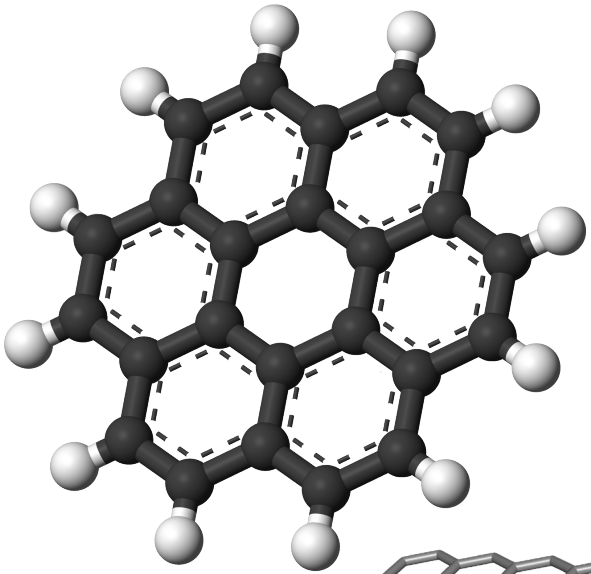
EXX + RPA @ DFT[2]

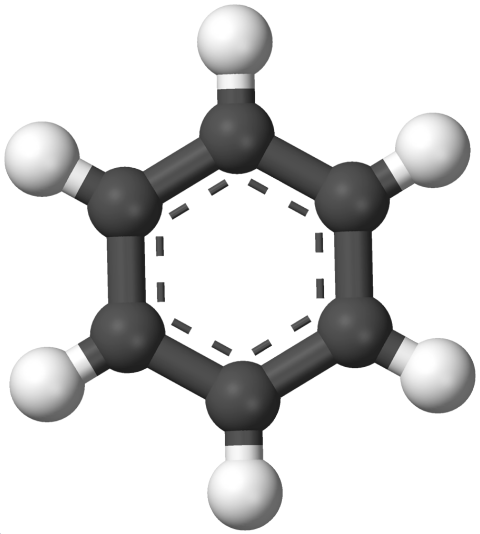
- χ_0 from delocalized molecular orbitals
\+ Works for all sorts of systems
– Costly numerical solution

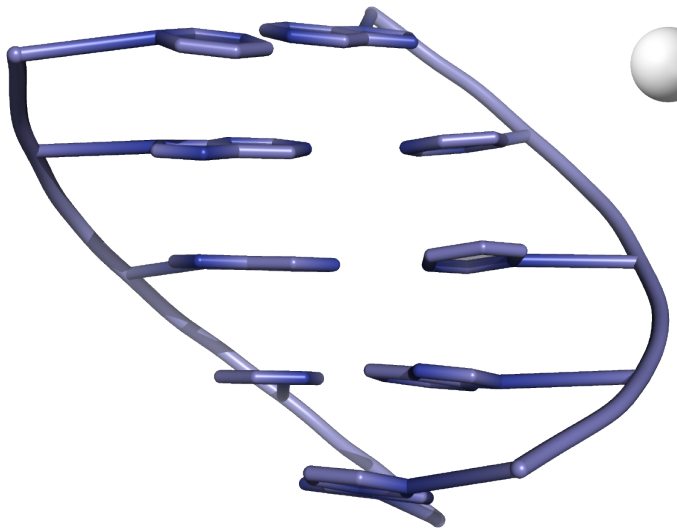
[1]Tkatchenko, DiStasio, Car, Scheffler, Phys. Rev. Lett. (2012)
[2]Zhu, Toulouse, Savin, Ángyán, J. Chem. Phys. (2010) *and refs therein*

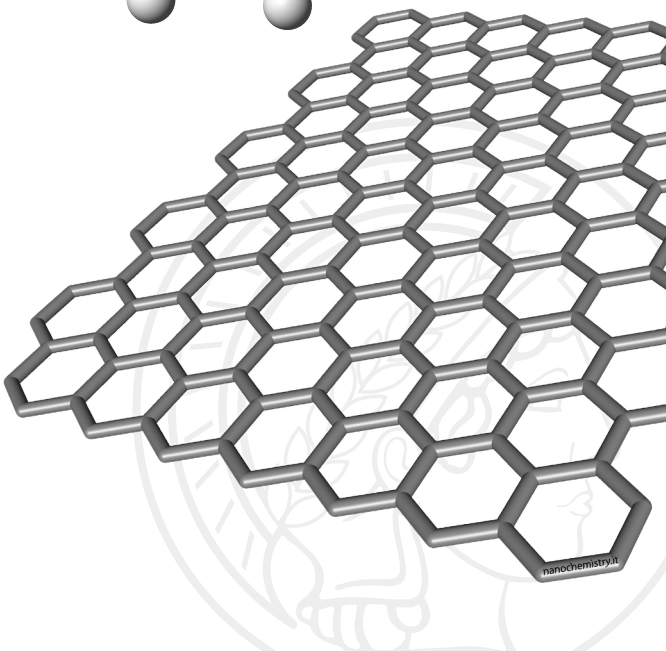
Benzene is a building element of many vdW systems



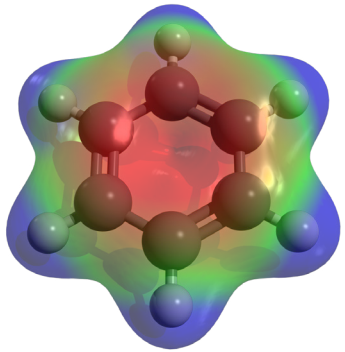


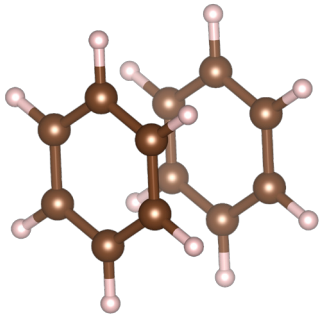


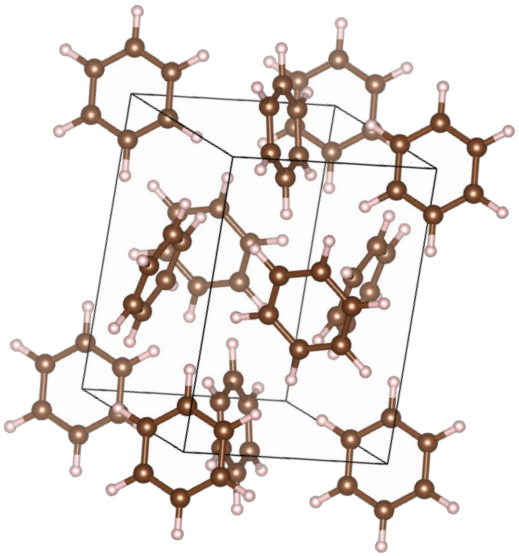




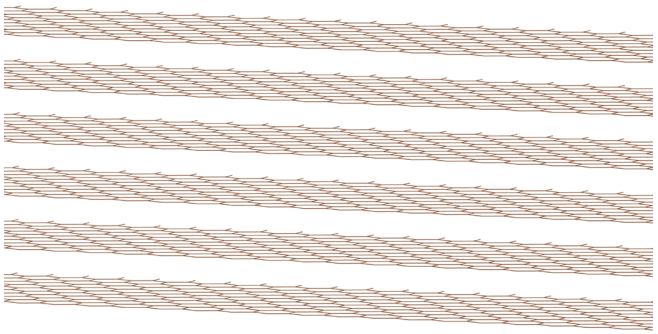
From benzene molecule to graphite

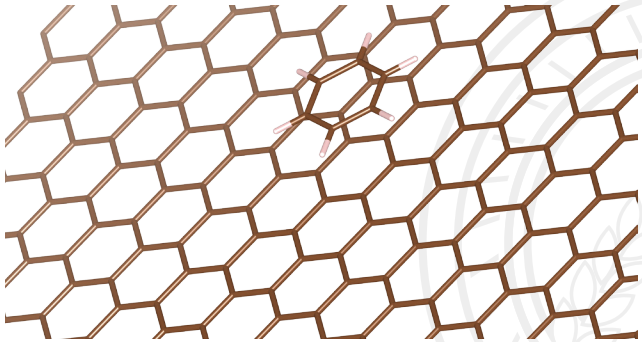






- Benzene molecule
- Benzene dimer
- Benzene crystal
- Benzene chain
- Benzene on graphene
- Graphene bilayer
- Graphene multilayer



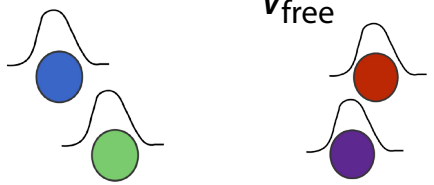


How many-body dispersion works

- Each atom replaced by oscillator with α from Tkatchenko–Scheffler

1

$$\alpha = \alpha_{\text{free}} \frac{V[n]}{V_{\text{free}}}$$

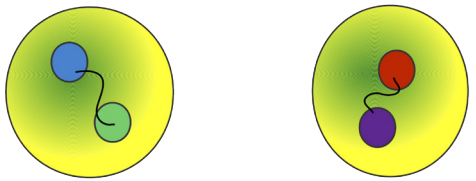


Self-consistent screening

- Response functions of near atoms interact

2

$$\tilde{\boldsymbol{\alpha}} = \boldsymbol{\alpha} - \boldsymbol{\alpha} \boldsymbol{T}_{<R} \tilde{\boldsymbol{\alpha}}$$

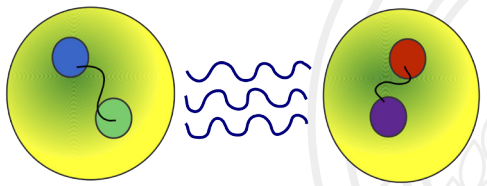


Random-phase approx

- Gives the long-range van der Waals energy
- Solved analytically

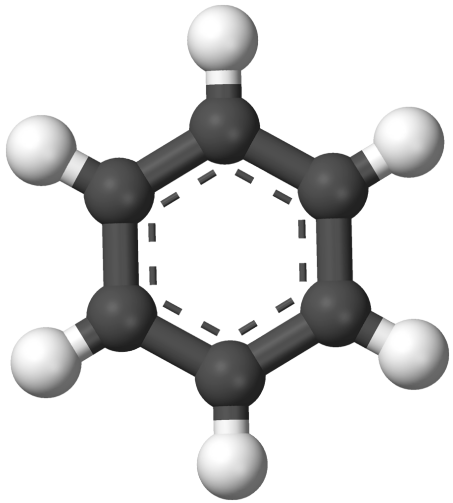
3

$$E_c = -\frac{1}{2\pi} \int_0^\infty \mathrm{d}\omega \sum_{n=2}^{\infty} \frac{1}{n} \mathrm{Tr}[(\tilde{\boldsymbol{\alpha}} \boldsymbol{T}_{>R})^n]$$



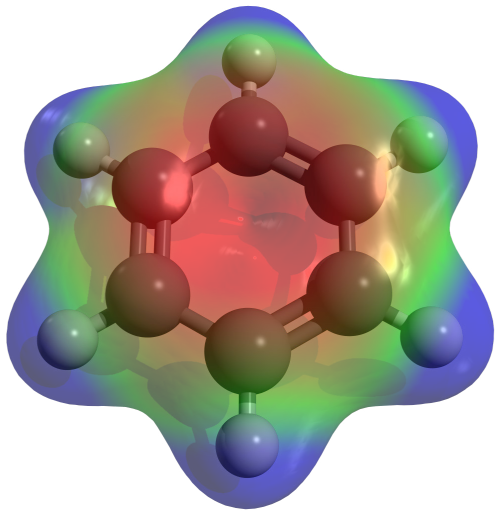
Non-empirical vdW methods provide more info

From empirical...



- no information beyond energy

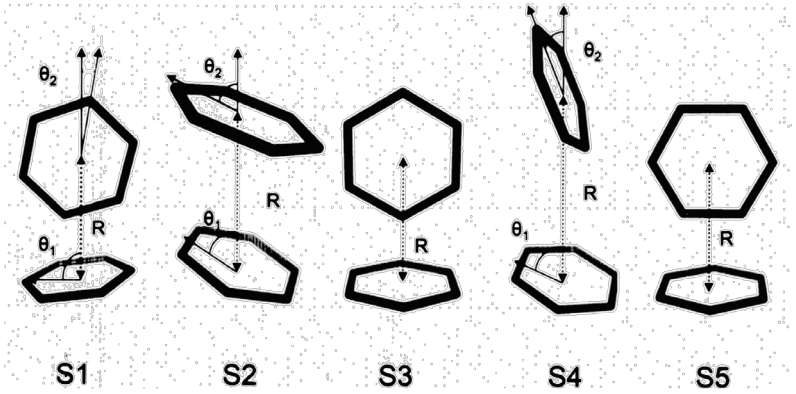
...to first principles



- polarizability
- anisotropy
- dipole fluctuation modes

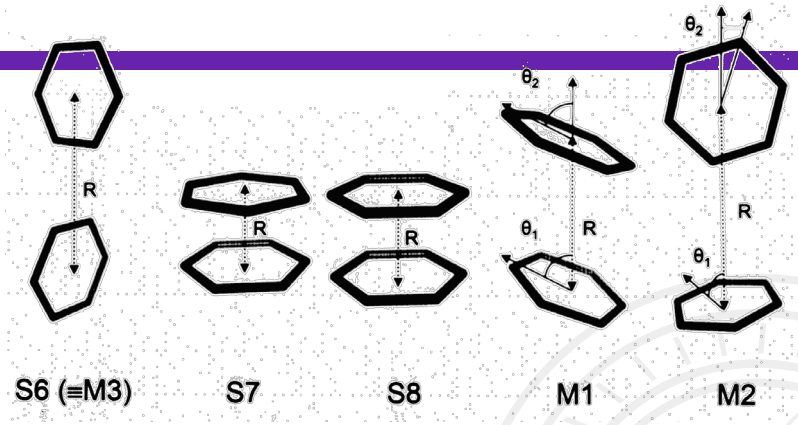
Structure is the starting point of most calculations

- Local minima on the potential energy surface
- Transition states
- Equilibrium structure (global minimum)



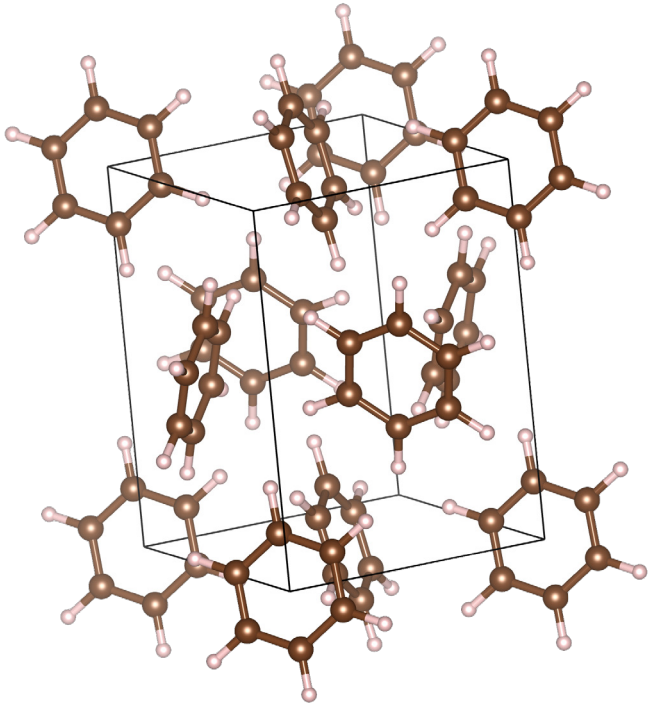
Benzene dimer

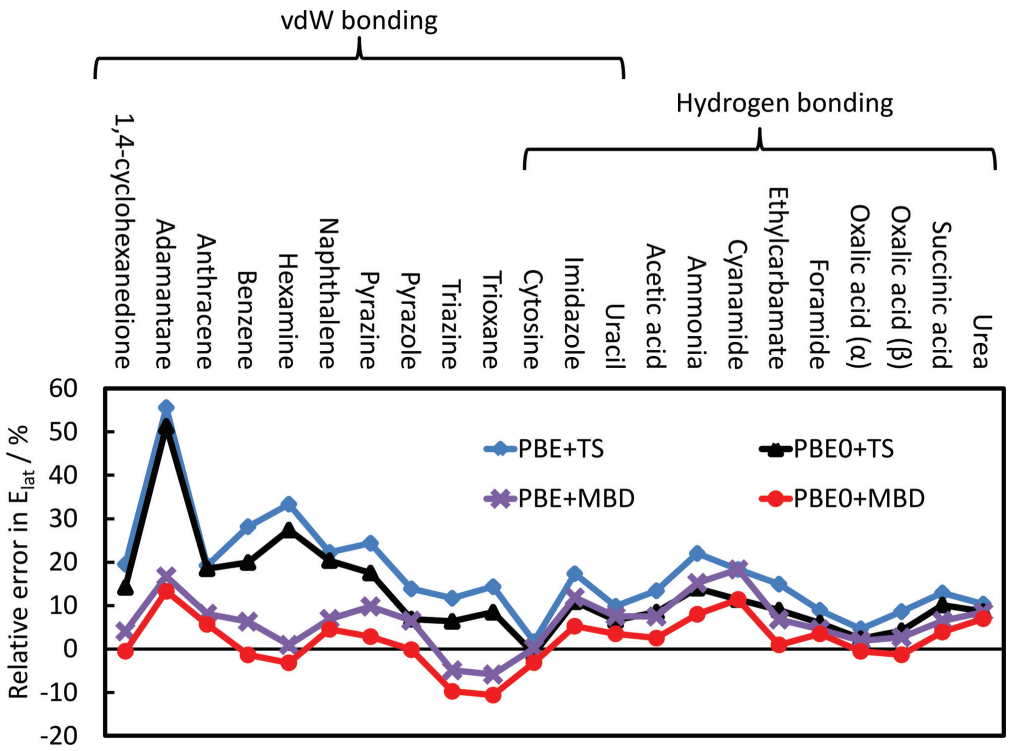
- Test case for van der Waals for decades
- Strong vdW interactions
- Quadrupole–quadrupole interactions
- Strong anisotropy



Many-body effects get interesting in crystals

- Many-body effects get amplified
- Multiple directions of interaction
- Anisotropy





Emergence of long-range fluctuations in low-dimensional systems

- It takes longer distances before many-body effects get saturated
- 2D systems: physisorption, interfaces
- 1D systems: self-assembly, quantum wires