Dispersion-corrected mean field electronic structure methods

Gerit Brandenburg <Gerit.Brandenburg@thch.uni-bonn.de> | 2016-09-22

MSSC2016: Ab initio Modelling in Solid State Chemistry - Imperial College London

London Centre for Nanotechnology
University College London

Outline of talk

1. Introduction and history
2. Perturbation theory at long-range
3. C6 based dispersion correction
4. Typical applications and benchmarks

Understanding phenomena in nature

Why can a Gecko stick to a glass wall?

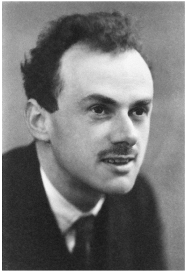
- effect cannot be explained by classical mechanics
- coupled zero-point fluctuations lead to attractive force

Why does a tablet change its properties?

- van der Waals interaction stabilize pill dependent on its form
- relevant for production process and dosage

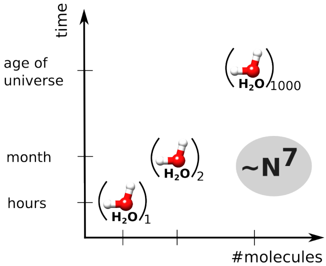
Exact simulation of biological systems computationally too demanding

Paul Adrian Maurice Dirac (1902-1984)



"The underlying physical laws (...) of a large part of physics and the ***whole of chemistry*** *are thus completely known,*

and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"[1]

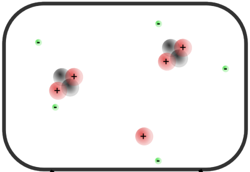


---

[1] P. A. M. Dirac, Proc. Roy. Soc.Ser. A, 1929, 123, 714 *Proc. Roy. Soc.Ser. A* **123**, 714 (1929)

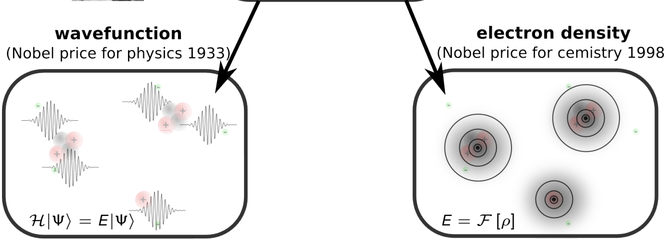
Possible theoretical ansatz

electronic system



Erwin Schrödinger
(1887-1961)

Walter Kohn
(1923-2016)



wavefunction
(Nobel price for physics 1933)

electron density
(Nobel price for cemistry 1998)

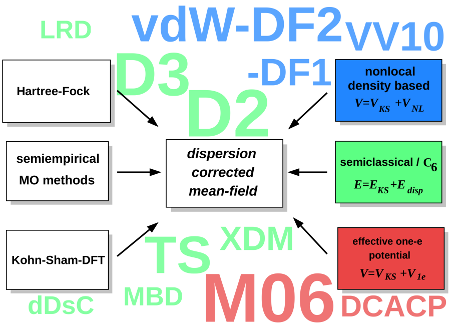
exact in principle,
complicated to solve

semi-local approximation
easier to solve

Semi-local density functionals cannot describe van der Waals interaction

	wavefunction	**density functional**
Pauli exchange repulsion	✓	✓
electrostatic	✓	✓
induction	✓	✓
London dispersion	✓	✗
computational cost	✗	✓
possible solutions	reduce comp. time with numerical tricks	include correction terms for vdW interaction

Focus on semi-classical corrections



LRD

vdW-DF2

VV10

D3

-DF1

D2

Hartree-Fock

nonlocal density based
$V=V_{KS}+V_{NL}$

semiempirical MO methods

dispersion corrected mean-field

semiclassical / C_6
$E=E_{KS}+E_{disp}$

Kohn-Sham-DFT

TS

XDM

effective one-e potential
$V=V_{KS}+V_{1e}$

dDsC

MBD

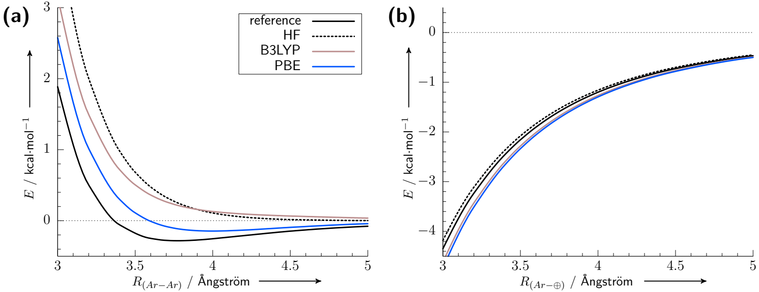
M06

DCACP

Recommended literature:

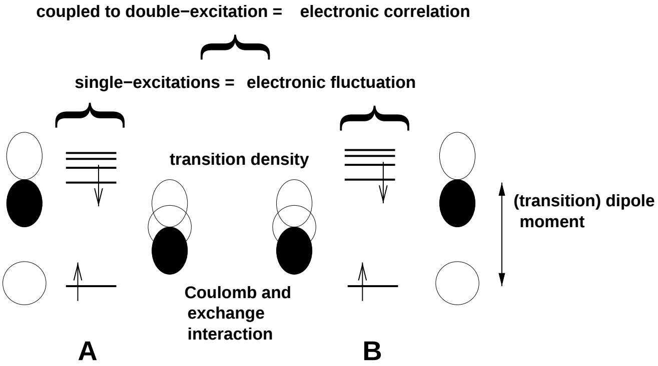
- A. Stone *The Theory of Intermolecular Forces*; Oxford University Press: Oxford, (1997)
- I. Kaplan *Intermolecular Interactions*; J. Wiley & Sons: Chichester, (2006)
- S. Grimme, A. Hansen, JGB, C. Bannwarth *Dispersion-corrected mean field electronic structure methods*; Chem. Rev. **116**, 5105 (2016)

The problem: empirical observation



- (a) rare gas dimer: lack of attraction in all DFA
- (b) rare gas – q: overpolarization of GGA DFA
- PES done with aug-cc-pV5Z, reference at CCSD(T) level

The problem: WFT picture



coupled to double−excitation = electronic correlation

single−excitations = electronic fluctuation

transition density

(transition) dipole moment

Coulomb and exchange interaction

A

B

$$E_{disp}^{(2)} = -\sum_{ia}\sum_{jb}\frac{(ia|jb)[(ia|jb)-(ib|ja)]}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j} \qquad (1)$$

Assumption and general strategy

Separated fragments *A* and *B* with non-overlapping densities

- Hamiltonian $H = H_0^A + H_0^B + V'$
- perturbation $V' = \int \mathrm{d}r\,\mathrm{d}r'\,\frac{\hat{\rho}^A(r)\hat{\rho}^B(r')}{|r - r'|}$
- eigenfunctions of fragments Ψ_n^A, Ψ_m^B
- eigenfunctions of unperturbed system direct product $\Psi_m^A \times \Psi_n^B$
- no antisymmetrization required, write as ket $|mn\rangle$

(1) perform perturbation theory to second (or higher) order

(2) expand perturbation V' in multipoles

Rayleigh-Schrödinger PT2

(1) Rayleigh-Schrödinger perturbation to second order

$$W^{AB} = W_0^{AB} + W_1^{AB} + W_2^{AB} + \mathcal{O}(3) \tag{2}$$

$$W_0^{AB} = W_0^A + W_0^B \tag{3}$$

$$W_1^{AB} = \langle 00|V'|00\rangle \tag{4}$$

$$\begin{aligned} W_2^{AB} &= -\sum_{mn}{}' \frac{\langle 00|V'|mn\rangle\langle mn|V'|00\rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \\ &= -\sum_{m}{}' \frac{\langle 00|V'|m0\rangle\langle m0|V'|00\rangle}{W_0^A - W_m^A} - \sum_{n}{}' \frac{\langle 00|V'|0n\rangle\langle 0n|V'|00\rangle}{W_0^B - W_n^B} \\ &\quad - \sum_{mn}{}'' \frac{\langle 00|V'|mn\rangle\langle mn|V'|00\rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \end{aligned} \tag{5}$$

Rayleigh-Schrödinger PT2

(1) Rayleigh-Schrödinger perturbation to second order

(a) Electrostatic in first order

$$\begin{aligned} U_{es}^{AB} &= \langle 00 | V' | 00 \rangle \\ &= \left\langle 00 \quad \left| \int \mathrm{d}r \, \mathrm{d}r' \, \frac{\hat{\rho}^A(r) \hat{\rho}^B(r')}{|r - r'|} \right| \quad 00 \right\rangle = \int \mathrm{d}r \, \mathrm{d}r' \, \frac{\rho^A(r) \rho^B(r')}{|r - r'|} \end{aligned} \tag{6}$$

(b) Induction in second order

$$\begin{aligned} U_{ind}^A &= - \sum_m{}' \frac{\langle 00 | V' | m0 \rangle \langle m0 | V' | 00 \rangle}{W_0^A - W_m^A} \\ U_{ind}^B &= - \sum_n{}' \frac{\langle 00 | V' | 0n \rangle \langle 0n | V' | 00 \rangle}{W_0^B - W_n^B} \end{aligned} \tag{7}$$

Rayleigh-Schrödinger PT2

(1) Rayleigh-Schrödinger perturbation to second oder

(c) Dispersion in second order

$$U_{disp}^{AB} = - \sum_{mn}{}'' \frac{\langle 00 | V' | mn \rangle \langle mn | V' | 00 \rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \tag{8}$$

Multipole expansion

(2) Expand V' in Cartesian multipoles

$$\begin{aligned} V' = \; & \mathcal{T} q^A q^B + \mathcal{T}_\alpha \left(q^A \mu^B_\alpha - \mu^A_\alpha q^B \right) \\ & + \mathcal{T}_{\alpha\beta} \left(\frac{1}{3} q^A \Theta^B_{\alpha\beta} - \mu^A_\alpha \mu^B_\beta + \frac{1}{3} \Theta^A_{\alpha\beta} q^B \right) + \mathcal{O}(n^3) \end{aligned} \tag{9}$$

$$\mathcal{T}^n_{\alpha\beta\ldots\nu} = \nabla_\alpha \nabla_\beta \ldots \nabla_\nu \left(\frac{1}{R} \right) \tag{10}$$

more compact in spherical harmonics

$$V' = \; \mathcal{Q}^A_{l_1 m_1} \mathcal{T}_{l_1 m_1, l_2 m_2} \mathcal{Q}^B_{l_2 m_2} \tag{11}$$

summation over identical indices always implied

Multipole expansion in PT2

(1+2) For simplicity start with dipole-dipole term

$$
\begin{aligned}
U^{AB}_{disp} &= - \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{\langle 0_A 0_B | \mu^A_\alpha \mathcal{T}_{\alpha\beta} \mu^B_\beta | m_A n_B \rangle \langle m_A n_B | \mu^A_\gamma \mathcal{T}_{\gamma\delta} \mu^B_\delta | 0_A 0_B \rangle}{W^A_0 - W^A_m + W^B_0 - W^B_n} \\
&= - \mathcal{T}_{\alpha\beta} \mathcal{T}_{\gamma\delta} \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{\langle 0_A | \mu^A_\alpha | m_A \rangle \langle m_A | \mu^A_\gamma | 0_A \rangle \langle 0_B | \mu^B_\beta | n_B \rangle \langle n_B | \mu^B_\delta | 0_B \rangle}{W^A_0 - W^A_m + W^B_0 - W^B_n} \\
&= - \frac{2}{\pi} \mathcal{T}_{\alpha\beta} \mathcal{T}_{\gamma\delta} \int \mathrm{d}\omega \left[\sum_m{}' \frac{\omega^A_m \langle 0_A | \mu^A_\alpha | m_A \rangle \langle m_A | \mu^A_\gamma | 0_A \rangle}{{\omega^A_m}^2 + \omega^2} \right. \\
&\qquad \left. \times \sum_n{}' \frac{\omega^B_n \langle 0_B | \mu^B_\beta | n_B \rangle \langle n_B | \mu^B_\delta | 0_B \rangle}{{\omega^B_n}^2 + \omega^2} \right]
\end{aligned}
\tag{12}
$$

Use McLachlan integral identity to factorize energy denominator

$$
\frac{1}{A + B} = \frac{2}{\pi} \int \mathrm{d}\omega \, \frac{AB}{(A^2 + \omega^2)(B^2 + \omega^2)} \tag{13}
$$

Multipole expansion in PT2

(1+2) Identify dynamic polarizability

$$U_{disp}^{AB} = -\frac{2}{\pi} \mathcal{T}_{\alpha\beta} \mathcal{T}_{\gamma\delta} \int \mathrm{d}\omega \, \alpha_{\alpha\gamma}^{A}(i\omega) \, \alpha_{\beta\delta}^{B}(i\omega) \qquad (14)$$

Spherical averaging (exact for atoms)

$$U_{disp}^{AB} = -\frac{3}{\pi} \int \mathrm{d}\omega \, \overline{\alpha}^{A}(i\omega) \, \overline{\alpha}^{B}(i\omega) \times \frac{1}{R^6} = -\frac{C_6^{AB}}{R^6} \qquad (15)$$

Analogue for higher order terms, short-range damping

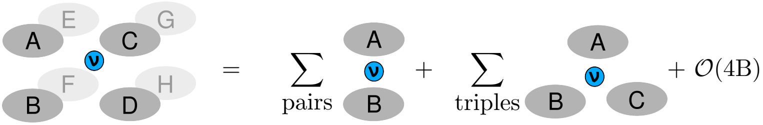
$$U_{disp}^{AB} = = \sum_{n=6,8,10,\ldots} \frac{C_n^{AB}}{R^n} f_{damp}^{(n)} \qquad (16)$$

More general via charge density susceptibility

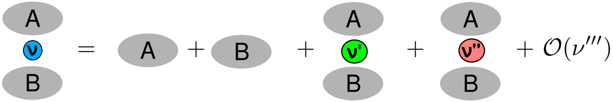
$$U_{disp}^{AB} = -\frac{1}{2\pi} \int \mathrm{d}\omega \int \mathrm{d}r_a \, \mathrm{d}r_a' \, \mathrm{d}r_b \, \mathrm{d}r_b' \, \frac{\chi(r_a, r_a', i\omega)\chi(r_b, r_b', i\omega)}{|r_a - r_b||r_a' - r_b'|} \qquad (17)$$

Summary long-range PT

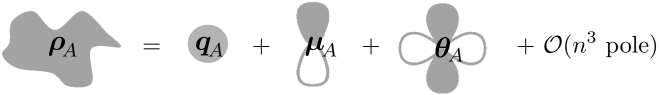
(1) multi-body expansion



(2) perturbation expansion



(3) multipole expansion



Method overview

D2 and D3 (S. Grimme)
TS and MBD (Tkatchenko-Scheffler)
XDM (Becke-Johnson)

Classifications of different methods according to

- order in many-body perturbation theory
- order in multipole expansion
- estimation and partitioning of C_6 coefficients
- shape of damping function

D2 (S. Grimme)

$$E_{disp}^{(D2)} = -\sum_{AB} \frac{C_6^{AB}}{R^6} f_{dmp}^{Fermi}(R) \tag{18}$$

$$C_6^{AB} = \sqrt{C_6^{AA} C_6^{BB}} \tag{19}$$

$$C_6^{AA} = \frac{N}{20} I_A \alpha_A(0) \tag{20}$$

- only atom-pairwise (two-body)
- lowest order multipoles
- C_6 estimated from ionization potential and static polarizability
- Fermi type zero damping[2]

---

[2] S. Grimme, *J. Comput. Chem.*, **27**, 1787 (2006)

D3 (S. Grimme)

$$E_{\text{disp}}^{(\text{D3})} = -\frac{1}{2}\sum_{n=6,8}\sum_{A,B}^{\text{atompairs}}\frac{C_n^{AB}}{r_{AB}^n}\cdot f_n^d(r_{AB}) - \frac{1}{6}\sum_{A,B,C}^{\text{atomtriples}}\frac{C_9^{ABC}\,(1+3\cos\theta_A\cos\theta_B\cos\theta_C)}{r_{ABC}^9}\cdot f_9^d(r_{ABC}) \qquad (21)$$

neglect all terms decaying faster than $\frac{1}{R^9}$

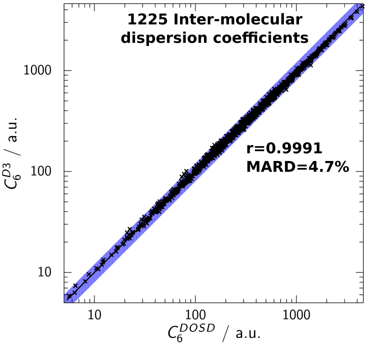
- third order in many-body expansion
- quadrupole terms in multipole expansion
- C_6 calculated (for model systems) via TD-DFT partitioned to atoms via fractional coordination number
- rational Becke-Johnson damping[3,4]

---

[3] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, **132**, 154104 (2010)

[4] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.*, **32**, 1456 (2011)

Semi-classical correction yields highly accurate dispersion coefficients



- Casimir-Polder integration of TD-DFT excitations on model hydrides

$$C_6^{\alpha\beta} = -\frac{3}{\pi}\int_0^\infty \alpha^\alpha(i\omega)\alpha^\beta(i\omega)\,\mathrm{d}\omega$$

- dipole oscillator strength distributions yield experimental C_6 (compilation by A. Tkatchenko)
- residual long-range error of D3 $<$ 5%[5,6]

---

[5] S. Grimme, *WIREs Comput. Mol. Sci.* **1**, 211-228 (2011)

[6] JGB, S. Grimme, *Top. Curr. Chem.* **345**, 1 (2014)

TS (Tkatchenko-Scheffler)

$$E_{disp}^{(TS)} = -\sum_{AB} \frac{C_6^{AB}}{R^6} f_{dmp}^{Fermi}(R) \tag{22}$$

$$C_6^{AB} = \frac{2 C_6^{AA} C_6^{BB}}{(\alpha^B(0)/\alpha^A(0)) C_6^{AA} + (\alpha^A(0)/\alpha^B(0)) C_6^{BB}} \tag{23}$$

$$C_6^{AA} = \frac{V_{eff}^A}{V_{free}^A} C_{6,free}^{AA} \tag{24}$$

- only atom-pairwise (two-body)
- lowest order multipoles
- C_6 estimated from effective atomic volumes
- Fermi type zero damping[7]

---

[7] A. Tkatchenko, M. Scheffler, *Phys. Rev. Lett.*, **102**, 073005 (2009)

TS+MBD (Tkatchenko-Scheffler)

$$E_{disp}^{(TS+MBD)} = \frac{1}{2}\sum_{p=1}^{3N}\sqrt{\lambda_p} - \frac{3}{2}\sum_{A}^{N}\omega_A^{TS+SCS} \tag{25}$$

$$V_{CFDM} = \sum_{A\neq B}^{N}\sum_{p\in A}^{3}\sum_{q\in B}^{3}\chi_p\tau_{pq}^{LR}\chi_q \tag{26}$$

$$\tau_{pq}^{LR} = \nabla_p \otimes \nabla_q W'(R) \tag{27}$$

- all many body orders (coupled fluctuating dipole Hamiltonian)
- lowest order multipoles
- C_6 estimated from screened effective atomic volumes
- Fermi type zero damping[8]

---

[8] A. Tkatchenko, R. A. DiStasio, R. Car, M. Scheffler, *Phys. Rev. Lett.*, **108**, 236402 (2012)

XDM (Becke-Johnson)

$$E_{\text{disp}}^{(\text{XDM})} = -\frac{1}{2} \sum_{n=6,8,10} \sum_{A,B}^{\text{atompairs}} \frac{C_n^{AB}}{r_{AB}^n} \cdot f_n^d(r_{AB}) \tag{28}$$

$$h_{X,\sigma}(r_1, r_2) = -\frac{1}{\rho_\sigma(r_1)} \sum_{ij} \phi_{i\sigma}(r_1)\phi_{j\sigma}(r_1)\phi_{i\sigma}(r_2)\phi_{j\sigma}(r_2) \tag{29}$$

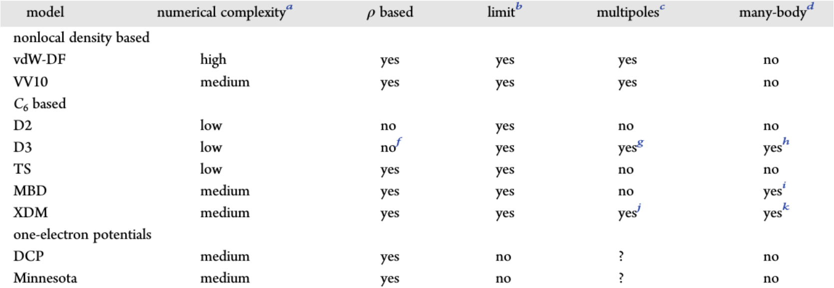
$$C_6^{AB} = \frac{\langle\mu_X^2\rangle_A \langle\mu_X^2\rangle_B \alpha_A^0 \alpha_B^0}{\langle\mu_X^2\rangle_A \alpha_B^0 + \langle\mu_X^2\rangle_B \alpha_A^0} \tag{30}$$

- lowest order in many-body expansion (higher orders exist, but are seldom used)
- quadrupole terms in multipole expansion
- C_6 calculated from exchange dipole
- rational Becke-Johnson damping[9]

---

[9] A. D. Becke, E. Johnson, *J. Chem. Phys.*, **123**, 154101 (2005)

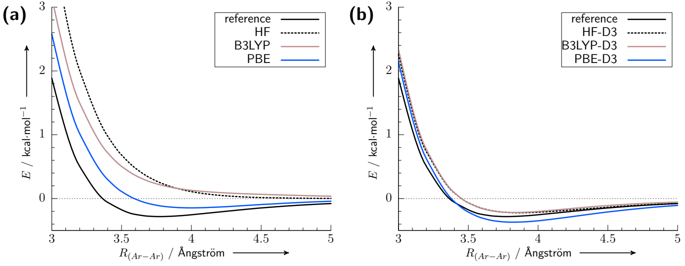
Summary C_6 based dispersion



model	numerical complexity[a]	ρ based	limit[b]	multipoles[c]	many-body[d]
nonlocal density based					
vdW-DF	high	yes	yes	yes	no
VV10	medium	yes	yes	yes	no
C_6 based					
D2	low	no	yes	no	no
D3	low	no[f]	yes	yes[g]	yes[h]
TS	low	yes	yes	no	no
MBD	medium	yes	yes	no	yes[i]
XDM	medium	yes	yes	yes[j]	yes[k]
one-electron potentials					
DCP	medium	yes	no	?	no
Minnesota	medium	yes	no	?	no

from S. Grimme, A. Hansen, JGB, C. Bannwarth, *Chem. Rev.* **116**, 5105 (2016)

Rare gas dimer ’problem’ solved



- all the presented methods can accurately describe the potentials of rare gas dimers

Multilevel methodologies

	basis set	DISP	BSSE	additional
TPSS-D3	'CBS'	$D3^{atm}$	–	–
$\Downarrow \times 10^1$ speed-up				
PBEh-3c[10] & **HSE-3c**[11]	DZ	$D3^{atm}$	gCP	mod. E_{XC}
$\Downarrow \times 10^1$				
HF-3c[12]	minimal	$D3^{atm}$	gCP	SRB
$\Downarrow \times 10^2$				
DFTB3-D3[13]	minimal	$D3^{atm}$	–	HX-damping, SK splines

---

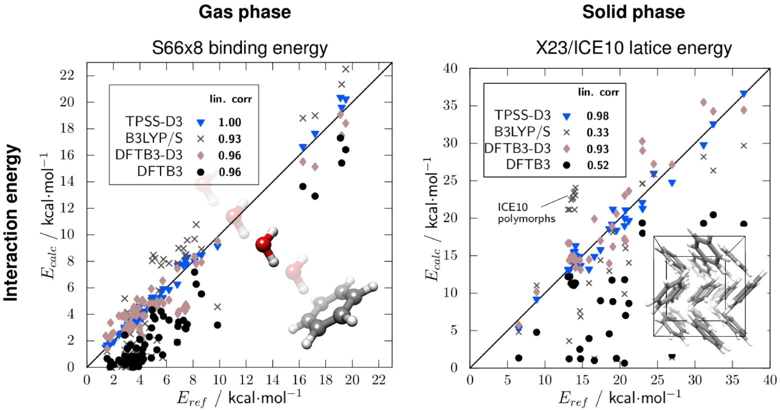
[10] S. Grimme, JGB, C. Bannwarth, A. Hansen, *J. Chem. Phys.*, **143**, 054107 (2015)

[11] JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.*, **18**, 15519 (2016)

[12] M. Cutini, B. Civalleri, M. Corno, R. Orlando, JGB, L. Maschio, P. Ugliengoa, *J. Chem. Theory Comput.*, **12**, 3340 (2016)

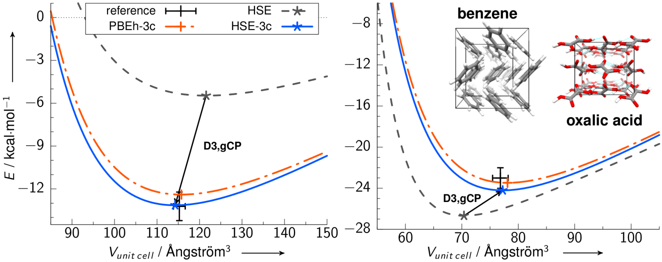
[13] JGB, S. Grimme, *J. Phys. Chem. Lett.* **5**, 1785 (2014)

Benchmark noncovalent interactions



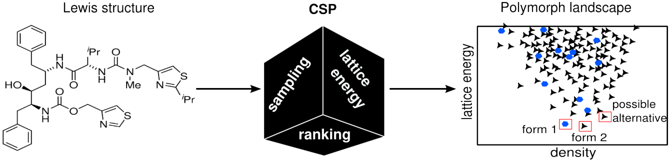
- gas phase: S66x8 with theoretical reference interactions
- solid phase: X23/ICE10 with back-corrected sublimation enthalpies

Description of simple organic crystals close to reference accuracy



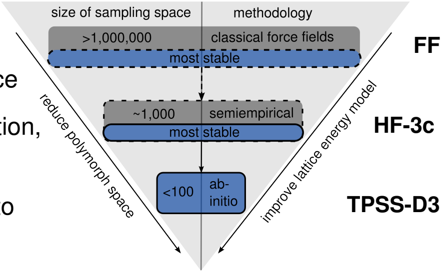
- error compensation between missing dispersion and BSSE is not reliable
- Identified by Computational Chemistry Highlights:
  "Most striking is the roughly 'MP2-quality' (...) obtained for non-covalent complexes and equilibrium structures (...) for medium-sized organic molecules."

Crystal structure prediction challenge



Layers of complexity:

- molecular conformational space
- space groups (varying orientation, conformation, etc.)
- polymorph ranking according to free energy[20,21]

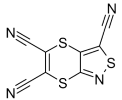


---

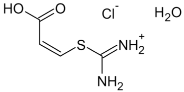
[14] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

[15] M. Neumann, F. Leusen, J. Kendrick, *Angew. Chem. Int. Ed.* **47**, 2427 (2008)

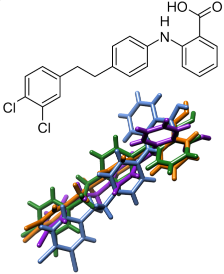
Promising results in the 6th blind test

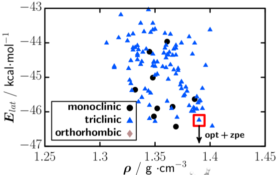


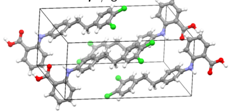
exp. polymorph: **Rank 1**
found in sampling: ✗



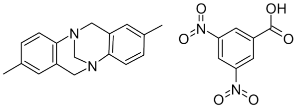
exp. polymorph: **Rank 1**
found in sampling: ✗



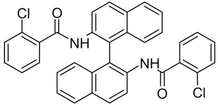




exp. polymorph: **Ranks 1-10**
found in sampling: ✓/ ✗



exp. polymorph: **Rank 1**
found in sampling: ✓



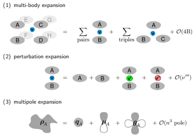
exp. polymorph: **Rank 1** found: ✗

---

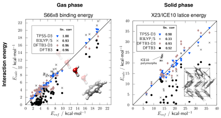
[16] A. Reilly, et al. *Acta Cryst. B*, **72**, 439 (2016) [17] JGB, S. Grimme *Acta Cryst. B*, **72**, 502 (2016)

Summary

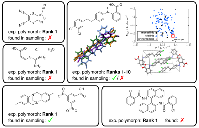
Take-home messages:



- London dispersion interaction arises in second order perturbation theory.
- C_6 based dispersion corrections are most efficient in DFT framework.



- Cost-effective methods show excellent performance for organic crystals.



- D3, gCP, HF-3c, HSE-3c, PBEh-3c implemented in CRYSTAL17