Organic crystal modeling:

On the importance of accurate London dispersion interactions

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CCMMP Seminars - Queen Mary - University of London, UK

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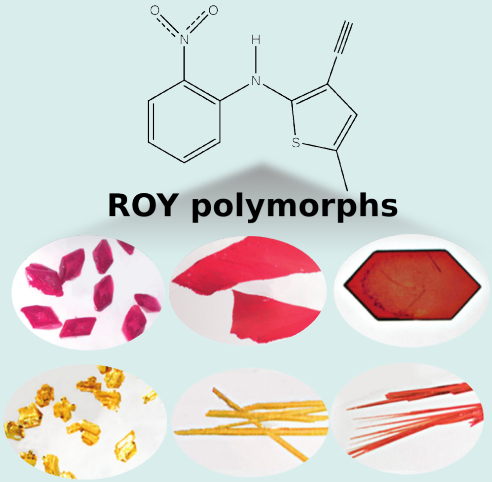
Outline of talk

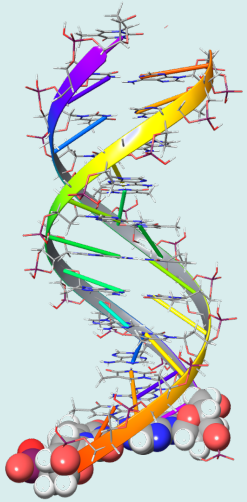
Large (periodic) systems with small energy gap are of interest

Physico-chemical properties depend on crystal packing?



- color indicates band gap $\sim 2\,\text{eV} - 2.5\,\text{eV}$
- available methods are either inaccurate or unfeasible

How to compute the electronic structure of biological mol.?



- large structures, typically in solution, small gaps by GGAs
- need for an accuracy semi-empirical methods cannot provide

Lessons learned in the past years

- good structures are the key to many important physical and chemical properties
- Kohn-Sham density functional theory is the method of choice for structures wavefunction methods may take over for energies
- sampling, entropy, solvation issues are more important than the last meV in electronic energy

Multilevel methodologies: finding the right compromise

	task/property	example method
accurate QM	single-point energy	DLPNO-CCSD(T), DMC (double) hybrid DFT
cheap QM	all	metaGGA (SCAN-D3[1]) HSE-3c[2,3]
very cheap QM	optimization/Hessians conformations	semi-empirical HF-3c[4,5], DFTB3-D3[6]
force field	dynamics conformational sampling	transferable or molecule specific (QM derived) FF

[1] JGB, J. E. Bates, J. Sun, J. P. Perdew *Phys. Rev. B*, **94**, 115144 (2016)

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

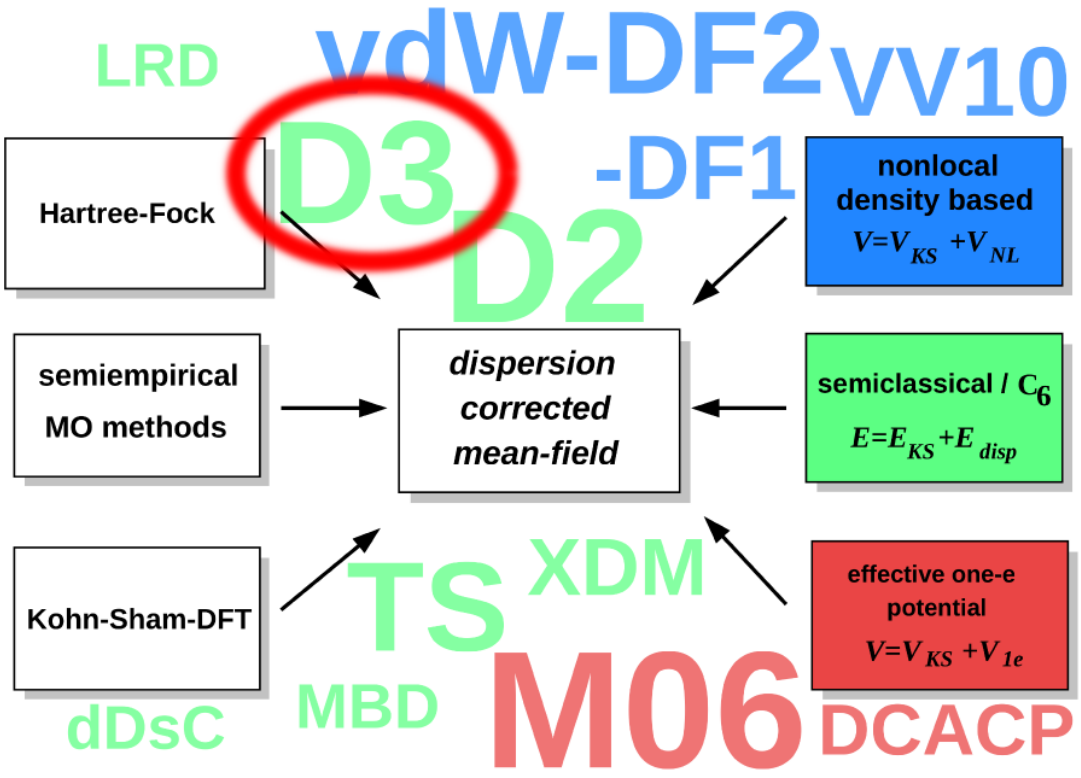
[3] JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.*, **18**, 15519 (2016)

[4] R. Sure, S. Grimme, *J. Comput. Chem.*, **34**, 1672 (2013) [5] JGB, S. Grimme, *Top. Curr. Chem*, **345**, 1 (2014)

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

Outline of talk

Many good dispersion corrections exist



- focus on D3 scheme as it can be used at all computational levels

[7] A. Stone *The Theory of Intermolecular Forces*; Oxford University Press: Oxford (1997)

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

Exact expression for correlation energy cannot be solve for realistic systems

$$E_c = -\frac{1}{2\pi}\int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \times \int_0^\infty \mathrm{d}\omega \left[\chi_\lambda(\mathbf{r},\mathbf{r}',i\omega) - \chi_0(\mathbf{r},\mathbf{r}',i\omega)\right]$$

- from adiabatic connection fluctuation dissipation theorem[9]
- by λ scaled Coulomb interaction
- dynamical charge density susceptibility

$$\chi_0(\mathbf{r},\mathbf{r}',i\omega) = -4\sum_i\sum_a \frac{\omega_{ai}}{\omega_{ai}^2+\omega^2}\varphi_i(\mathbf{r})\varphi_a(\mathbf{r})\varphi_a(\mathbf{r}')\varphi_i(\mathbf{r}')\,,$$

$\rightarrow$ approximation needed

[9] A. Zangwill, P. Soven, *Phys. Rev. A* **21**, 1561 (1980)

Coarse-graining to atomic contributions leads to significant simplifications

- coarse-grain to atomic contributions

$$\alpha_{ij}(i\omega) = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \mathbf{r}_i \mathbf{r}'_j \chi(\mathbf{r}, \mathbf{r}', i\omega)$$

- expansion of Coulomb operator in multipoles[10]

$$E_{\text{disp}}^{AB} = -\underbrace{\frac{3}{\pi}\int \mathrm{d}\omega\, \alpha_A(i\omega)\alpha_B(i\omega)}_{C_6^{AB}} \times \frac{1}{R_{AB}^6}$$

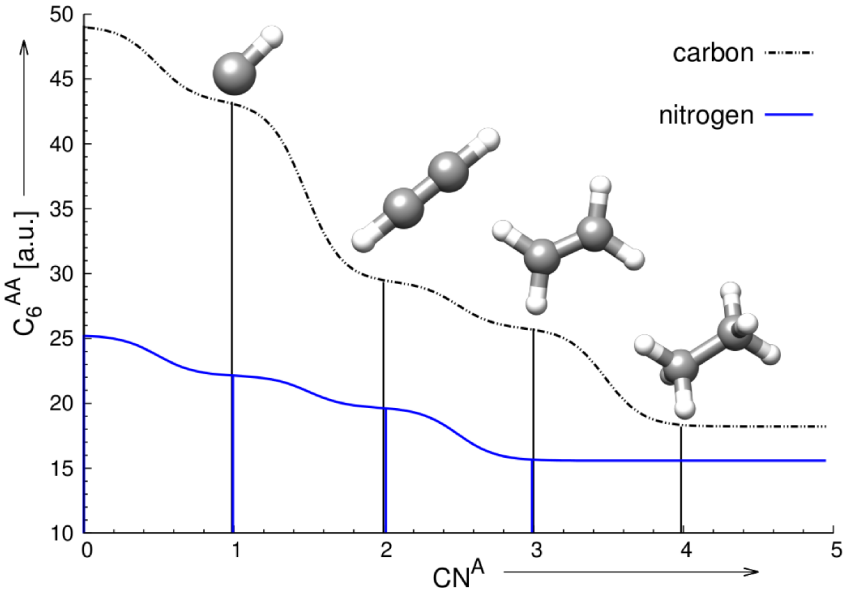
- C_8^{AB} and C_9^{AB} from recursion relations and averages[11]

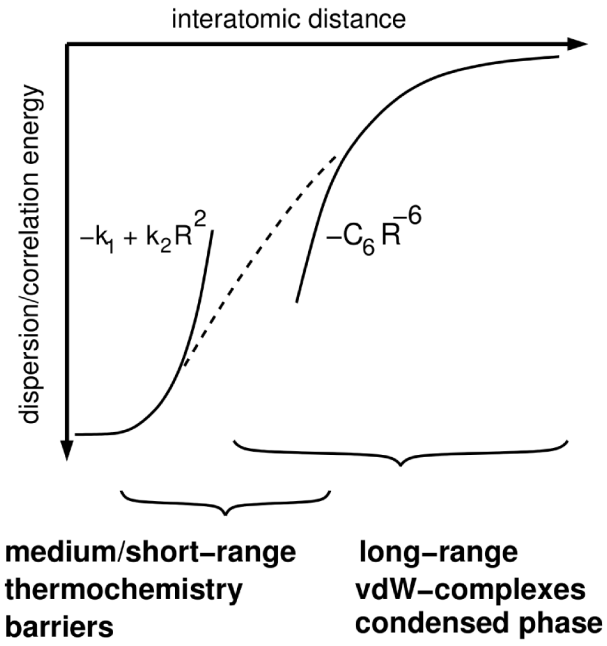
$$E_{\text{disp}}^{(\text{D3})} = -\frac{1}{2}\sum_{n=6,8}\sum_{A,B}^{\text{atoms}} \frac{C_n^{AB}}{R_{AB}^n} \cdot f_n^d(R_{AB}) - \frac{1}{6}\sum_{A,B,C}^{\text{atoms}} \frac{C_9^{ABC}}{R_{AB}^9} \cdot f_9^d(R_{ABC}, \theta_{ABC})$$

[10] H. B. G. Casimir. D. Polder, *Phys. Rev.* **73**, 360 (1948)

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

Geometric coordination number for interpolations of reference C_6

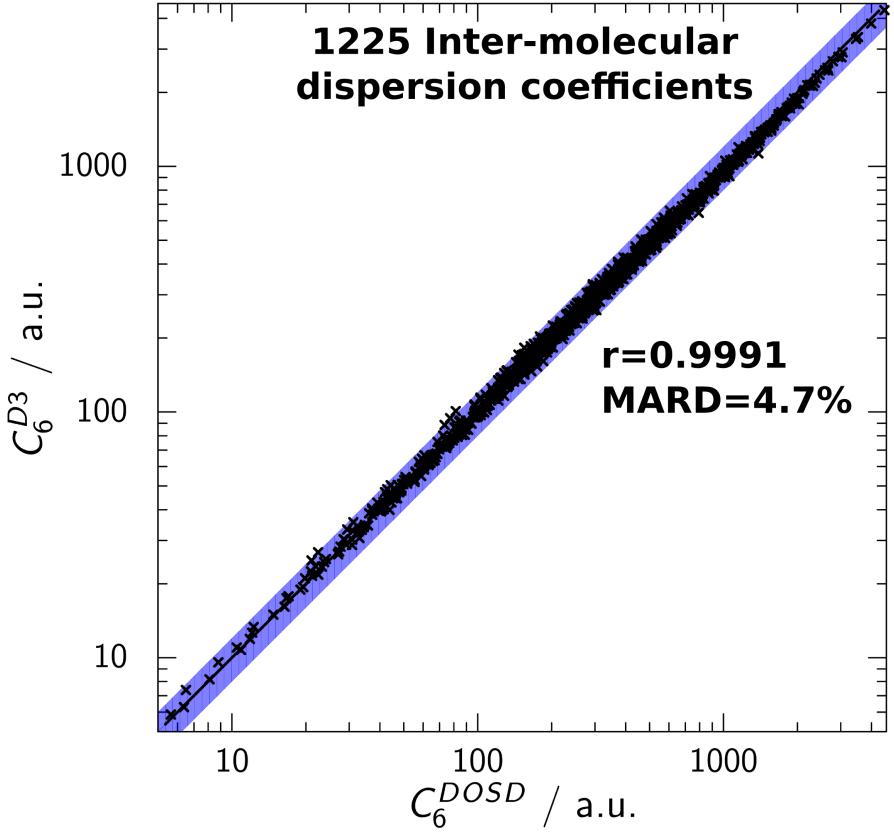




- atoms-in-molecules C_6 by TD-DFT of $\alpha(i\omega)$ on model hydrides
- reference C_6 are mapped to real system via geometrical coordination
- short-range damping avoids double counting[12]

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

Semi-classical scheme yields highly accurate dispersion coefficients



D3 correction

- dipole oscillator strength distribution yield $C_6^{\text{exptl.}}$ (compiled by A. Tkatchenko)
- residual long-range error of D3 $< 5\%$ [13]
- deviations are close to intrinsic TD-DFT errors of $\alpha(i\omega)$

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

Outline of talk

Requirements on the new density functional method

- reasonably fast for optimizations and frequencies
  $\rightarrow$ small atomic orbital expansion
- avoid most self-interaction error
  $\rightarrow$ use one-determinantal (Fock) exchange
- numerically robust including small gap solids
  $\rightarrow$ long-range screening of Fock exchange
- good, globally accurate PES
- accurate non-covalent interactions
- consistency for isolated molecules and the condensed phase

Three ingredients target different interaction regimes

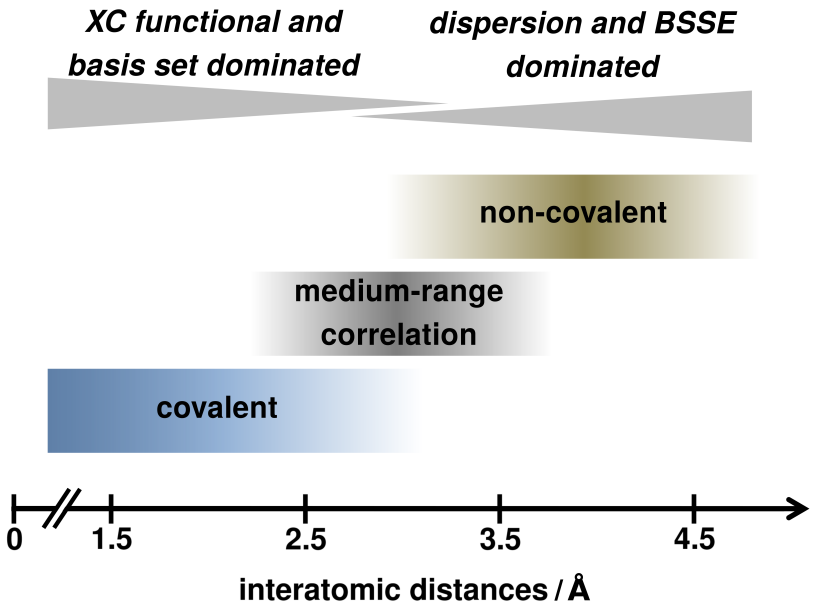
HSE-3c contributions[3]

$$E_{\text{tot}}^{\text{HSE-3c}} = E_{\text{xc}}^{(\text{modHSE})} + E_{\text{DISP}}^{(\text{D3})} + E_{\text{BSSE}}^{\text{gCP}}$$

(A) DFA/basis set
mod. HSE[14] / def2-mSVP[2]

(B) London DISP interaction
D3 correction

(C) BSSE counterpoise correction
gCP scheme



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

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

[14] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006)

Compromise of known functionals for exchange correlation functional

$$E_{\mathrm{xc}}^{(\mathrm{modHSE})} = \mathbf{a_x}\, E_{\mathrm{x}}^{(\mathrm{HF,SR})}(\omega) + (1 - a_x)\, E_{\mathrm{x}}^{(\mathrm{HSE,SR})}(\omega) + E_{\mathrm{x}}^{(\mathrm{HSE,LR})}(\omega) + E_{\mathrm{c}}^{(\mathrm{modPBE})}$$

- modified HSE to reproduce modified PBE-XC

$$F_X^{\mathrm{PBE}} = 1 + \frac{\mu s}{1 + \frac{\mu s^2}{\kappa}}, \qquad s = |\nabla\rho/\rho^{4/3}|$$

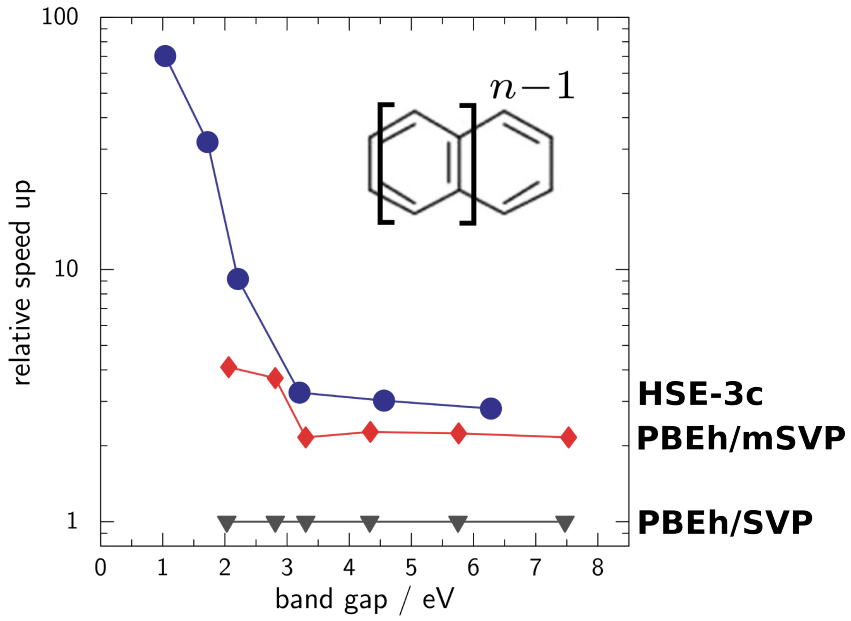
- μ from PBEsol, κ averaged from PBE/revPBE
- $\beta = 0.03$ in F_C^{PBE} fitted to atomization energies
- $a_x = 0.42$: getting bond length right (standard range-separation $\omega = 0.11$)
- mSVP atomic orbitals fixed and available for whole PES

$\rightarrow$ only **seven** globally fitted parameters

Large computational savings and numerically robust for small-gap solids

Series of oligoacene crystals

- substantial speedup due to small basis set
- short-range Fock exchange reduces SIE
- numerically robust at small band gaps

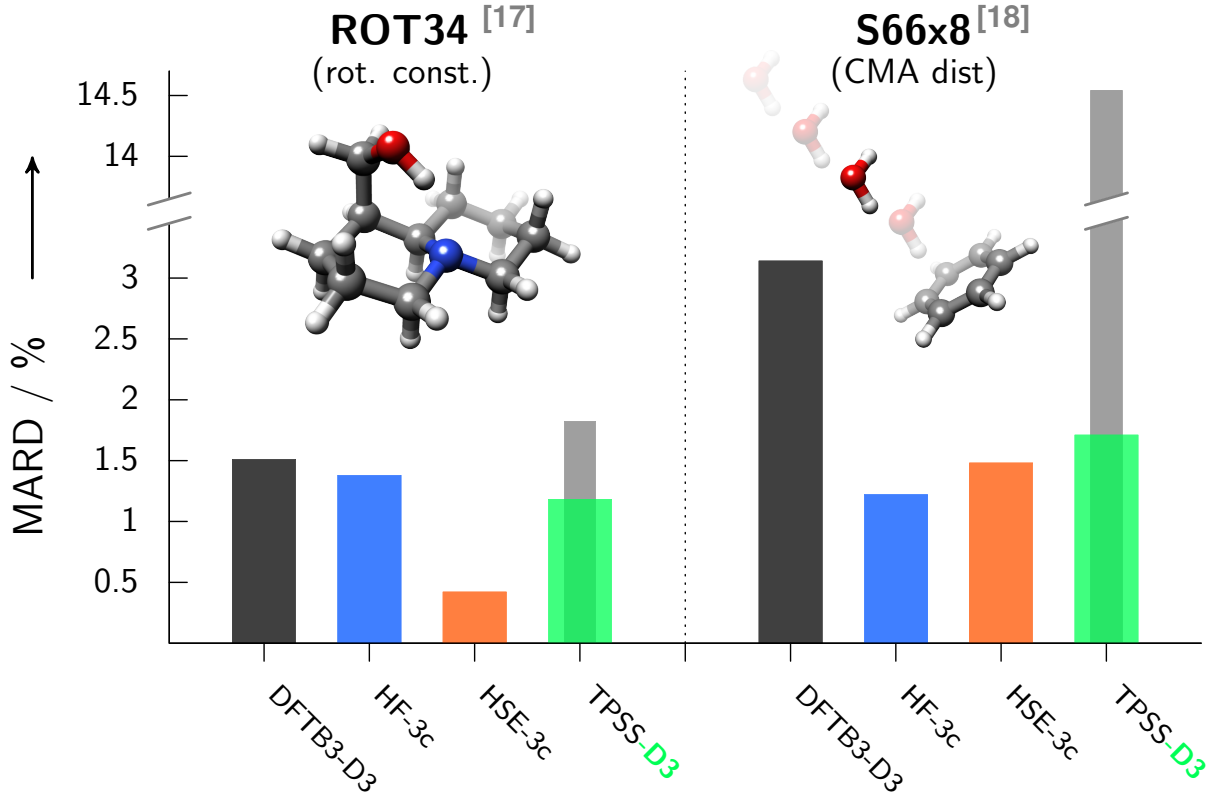


→ exploit rotational-translational symmetry within CRYSTAL[15,16]

[15] R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, et al., *Int. J. Quantum Chem.*, **114**, 1287 (2014)

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

Systematically improvable bond length and molecular structures

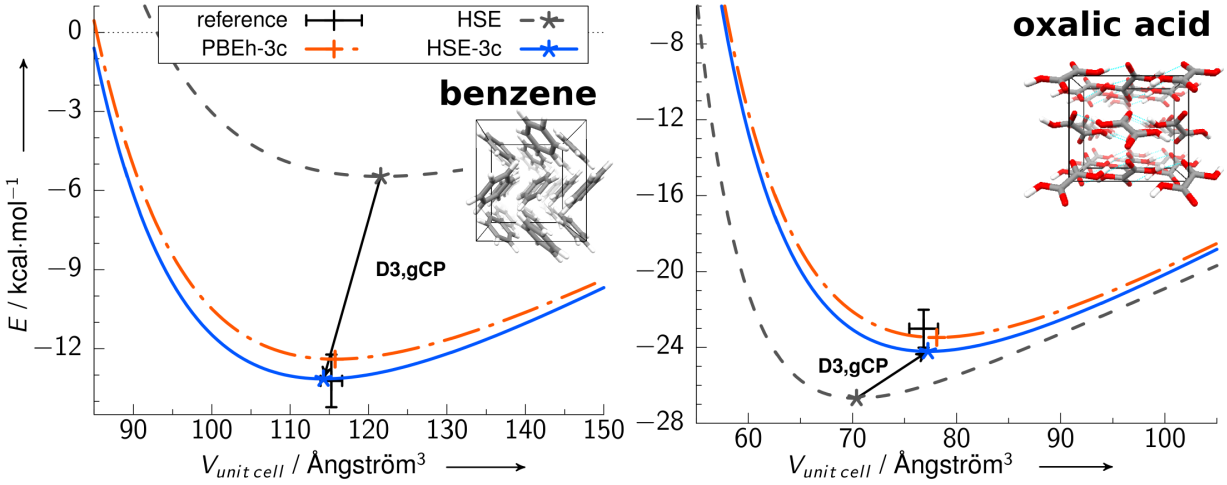


- significant effect of dispersion interaction

[17] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.*, **15**, 16031 (2013)

[18] J. Rezáč, K. Riley, P. Hobza, *J. Chem. Theory Comput.*, **8**, 2427 (2011)

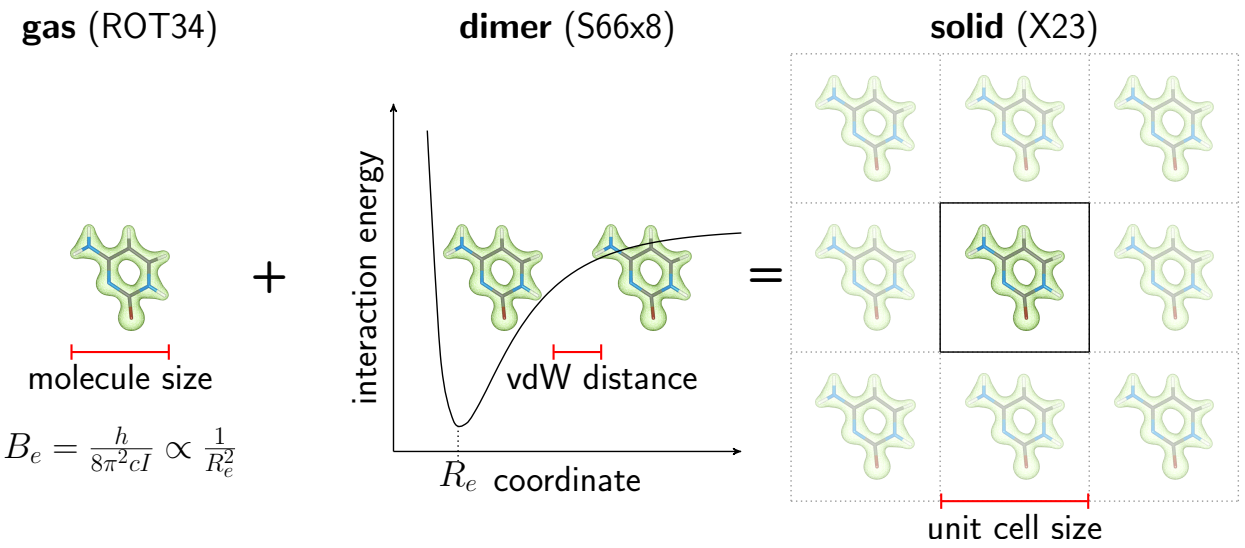
Description of simple organic crystals close to reference accuracy



- thermal corrections needed for equilibrium structure and lattice energy[11]
- 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."

[19] A. M. Reilly, A. Tkatchenko, *J. Chem. Phys.* **139**, 024705 (2013)

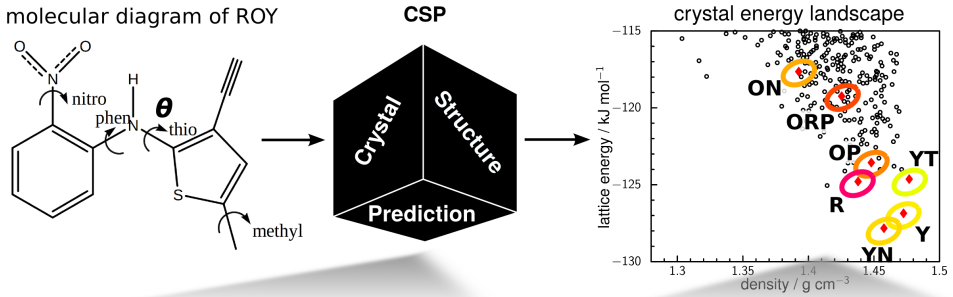
Consistency for structures achieved



	ROT34 org. mol.	**S66x8** non-covalent	**X23** molecular crystal
TPSS/large basis	1.9	14.6	27.9
TPSS-D3/large basis	1.3	1.3	1.0
HF-3c (very cheap QM)	1.5	-1.2	-5.7
DFTB3-D3 (very cheap QM)	1.2	-2.9	-12.6
HSE-3c (cheap QM)	**0.2**	**1.3**	**0.7**

mean of relative deviation in %

Crystal structure prediction challenge



Molecular conformational analysis
PBEh-3c or TB

↓

Initial generation of millions of crystal structures
transferable or tailored FF

↓

Hierarchical refinement of thousands of crystal structures based on lattice energy
HF-3c or TB

↓

Further thermodynamic refinement and property calculation on tens of structures
TPSS-D3 or HSE-3c

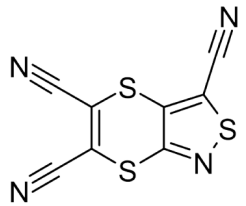
Properties
of ROY polymorphs

characterized	uncharacterized
Red prism *P*-1, θ=21.7°	
Orange **R**ed **P**late *P*bca, θ=39.4°	
Orange **P**late $P2_1/n$, θ=46.1°	
Orange **N**eedle $P2_1/c$, θ=52.6°	
Yellow **N**eedle *P*-1, θ=104.1°	
Yellow prism $P2_1/n$, θ=104.7°	
Yellow prism **T**ype 2 $P2_1/n$, θ=112.8°	

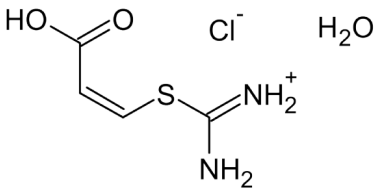
[20] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

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

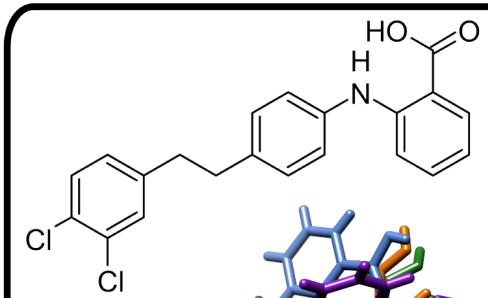
Promising results in the 6th blind test

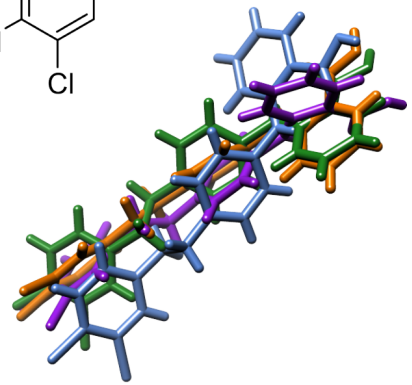


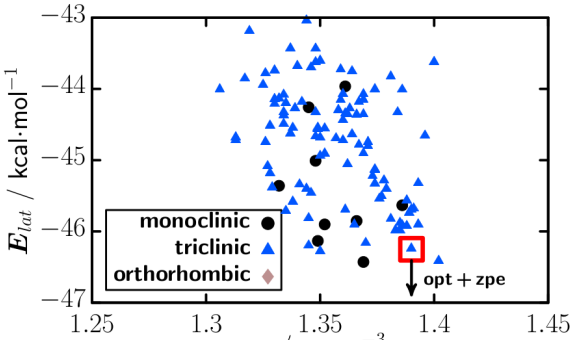
exp. polymorph: **Rank 1**
found in sampling: ✗

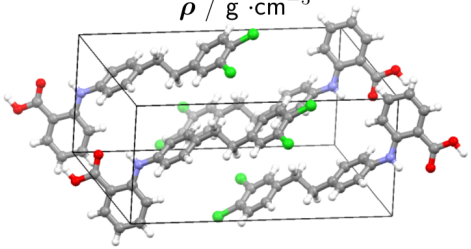


exp. polymorph: **Rank 1**
found in sampling: ✗

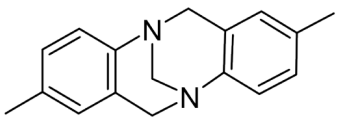


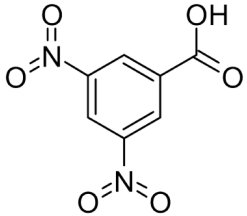




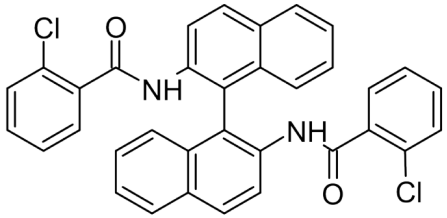


exp. polymorph: **Ranks 1-10**
found in sampling: ✓/ ✗





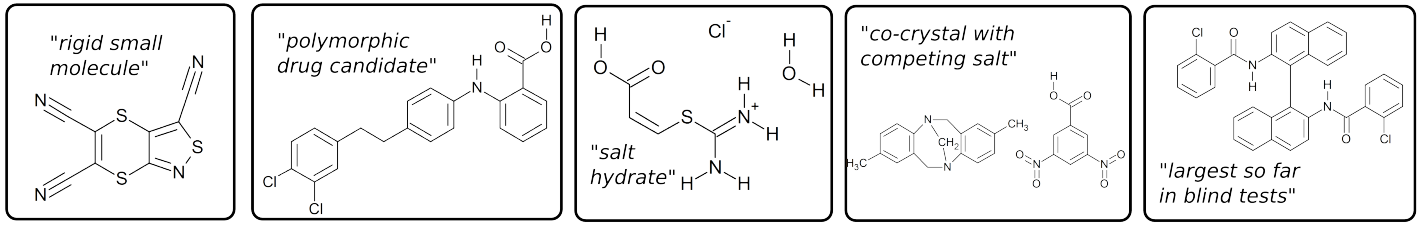
exp. polymorph: **Rank 1**
found in sampling: ✓



exp. polymorph: **Rank 1** found: ✗

[22] A. Reilly, et al. *Acta Cryst. B*, **72**, 439 (2016)

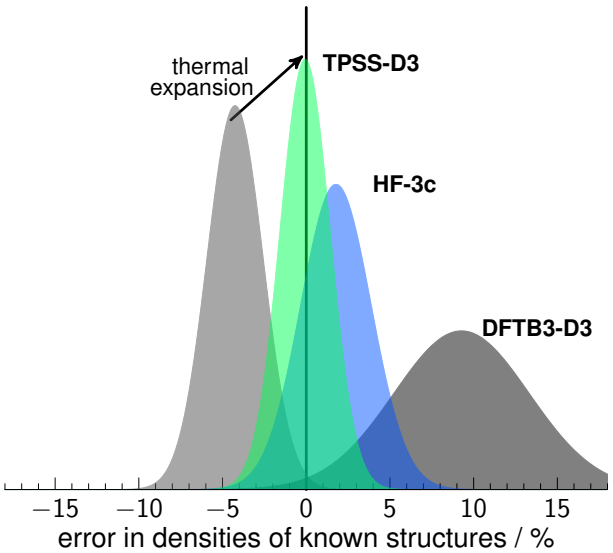
Is relative crystal stability easier?



- extract polymorph candidates from 6th CSP blind challenge[23]
- 9 known polymorphs + 10 diverse low energy hypothetical structures

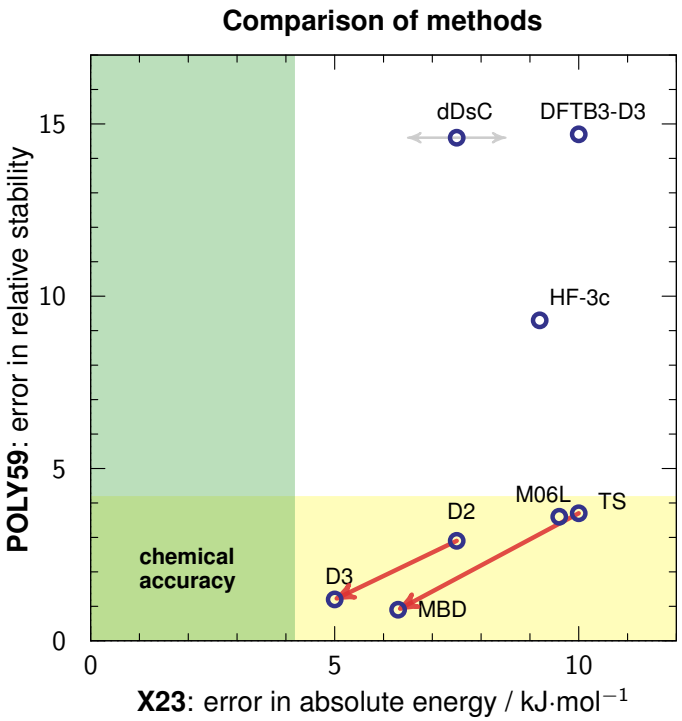
Assumptions

- thermodynamic minimum is measured
- $E_{\mathrm{latt}}(0\,\mathrm{K})$ enough for relative stability
- modeling of thermal expansion improves agreement between computed and measured crystal structures



[23] JGB, S. Grimme *Acta Cryst. B*, **72**, 502 (2016)

Error compensation less than hoped



- clear improvement with modern methods D2→D3 and TS→MBD
- gain factor 2-4 for relative stabilities reaching chemical accuracy
- several structures within 1 kJ/mol energy window

Remaining problems

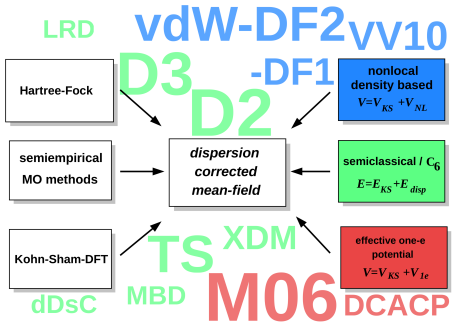
- ∼50 % of reported polymorphs are within 2 kJ/mol[24] → hard to distinguish
- neglected free energy contributions and kinetic effects ∼1-4 kJ/mol

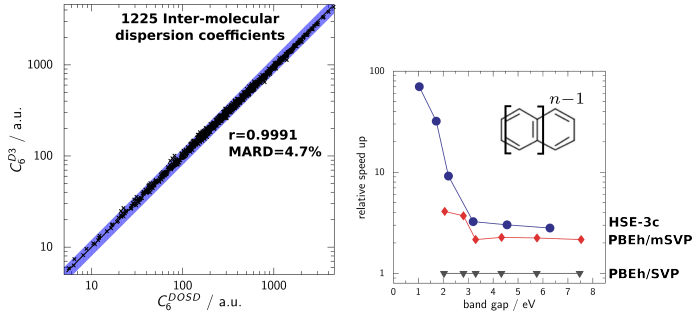
[24] A. J. Cruz-Cabeza, S. M. Reutzel-Edens, J. Bernstein *Chem. Soc. Rev.* **44**, 8619 (2015)

Summary

Conclusions

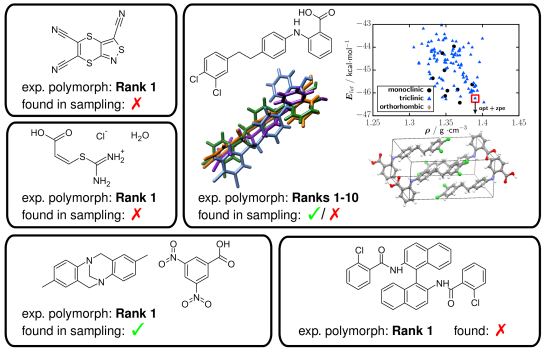
- cost-efficient method for routine electronic structure calculations needed
- HSE-3c is a promising new composite scheme
- good results in 6th CSP blind test





Outlook and possible improvements

- methods will be available in CRYSTAL17
- use quasi-harmonic treatment to map out full phase diagrams $\Delta G(T, P)$



Acknowledgements

Collaborators

- Stefan Grimme (Bonn)
- Sally Price (London)
- Angelos Michaelides (London)
- Felix Fernandez-Alonso (Harwell Oxford)
- Eike Caldeweyher (Bonn)
- Bartolomeo Civalleri (Torino)
- Roberto Orlando† (Torino)
- Anthony Reilly (Cambridge)

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Thanks

Key references

- Dispersion corrections:

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

- PBEh-3c and HSE-3c:

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

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

- DFA-DISP for crystal structure prediction:

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

  JGB, S. Grimme *Acta Cryst. B*, **72**, 502 (2016)

- homepage: **www.gerit-brandenburg.de**