A new screened exchange hybrid functional: Accurate and efficient structures and interaction energies

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STC2016 - 52ND SYMPOSIUM ON THEORETICAL CHEMISTRY - BOCHUM, GER

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Outline of talk

1 Introduction and motivation

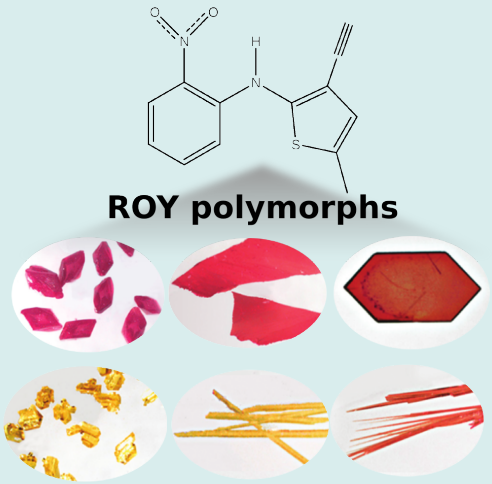
2 Design principles of HSE-3c

3 Application of HSE-3c to thermal expansion

4 Conclusions

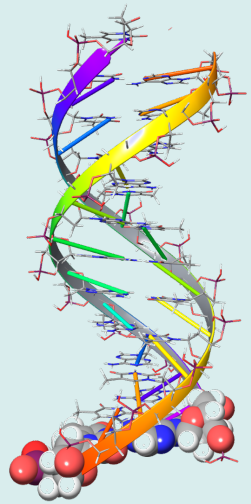
Large (periodic) systems with small energy gap are of interest

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

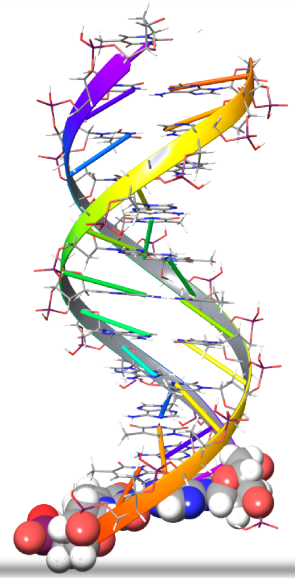
How to compute the electronic structure of biological mol.?



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

New density functional for cost-efficient electronic structure computation

	tight-binding	GGA	global hybrid
accuracy	✗	✗	✓
reduced SIE [1,2]	✗	✗	✓
num. robust	✓	✓	✗
comp. feasible	✓	✓	✗



→ need for an efficient and robust hybrid density functional

[1] J. P. Perdew, A. Zunger, *Phys. Rev. B*, **23**, 5048 (1981)

[2] A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993)

Three ingredients target different interaction regimes

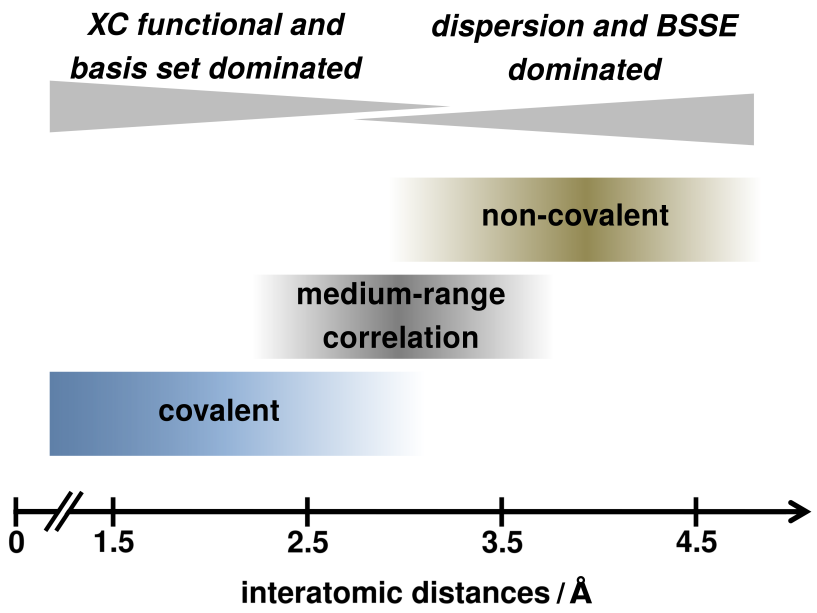
HSE-3c contributions[3]

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

(A) DFA/basis set
mod. HSE[4] / def2-mSVP[5]

(B) London DISP interaction

(C) BSSE counterpoise correction



$$E_{\text{xc}}^{(\text{modHSE})} = \mathbf{0.42}\, E_{\text{x}}^{(\text{HF,SR})}(\omega = \mathbf{0.11}) + 0.58\, E_{\text{x}}^{(\text{HSE,SR})}(\omega) + E_{\text{x}}^{(\text{HSE,LR})}(\omega) + E_{\text{c}}^{(\text{modPBE})}$$

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

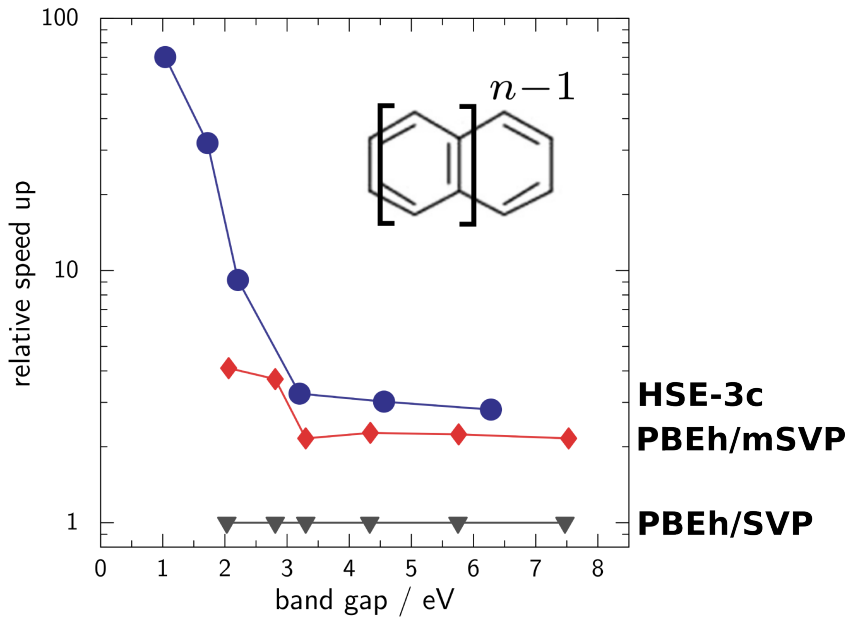
[4] J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006)

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

Substantial speed up due to efficient basis set and screened exchange

Series of oligoacene crystals

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

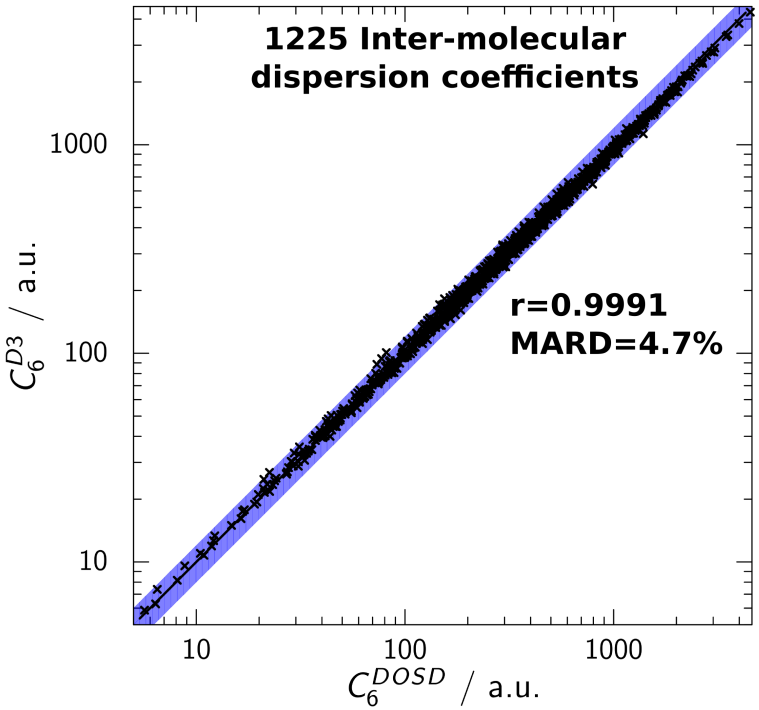


→ exploit rotational-translational symmetry within CRYSTAL[6,7]

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

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

Semi-classical correction yields highly accurate dispersion coefficients



D3 correction[8-10]

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

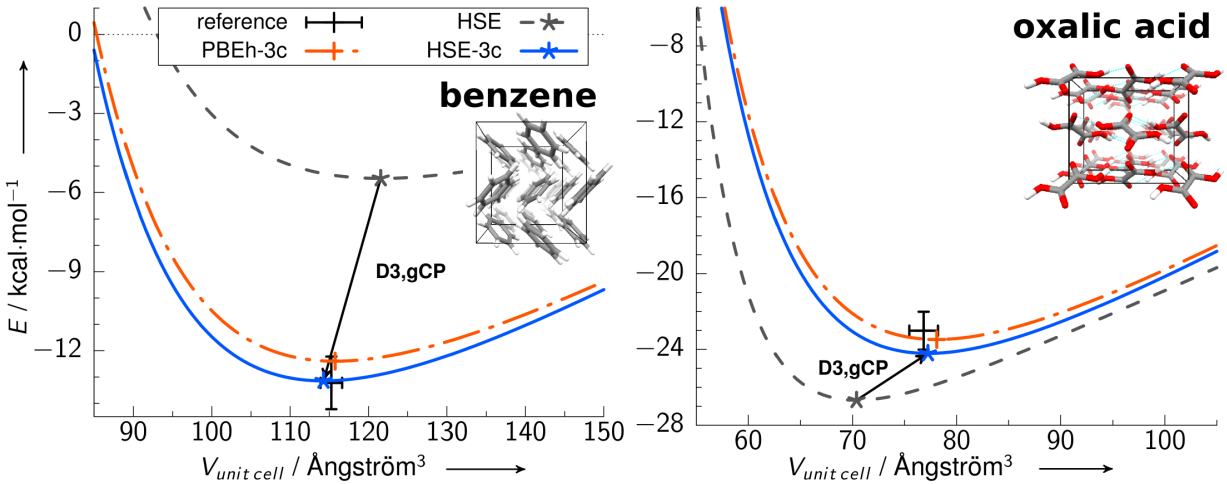
- Casimir-Polder integration of TD-DFT excitations on model hydrides
- residual long-range error $< 5\%$

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

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

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

Description of simple organic crystals close to reference accuracy

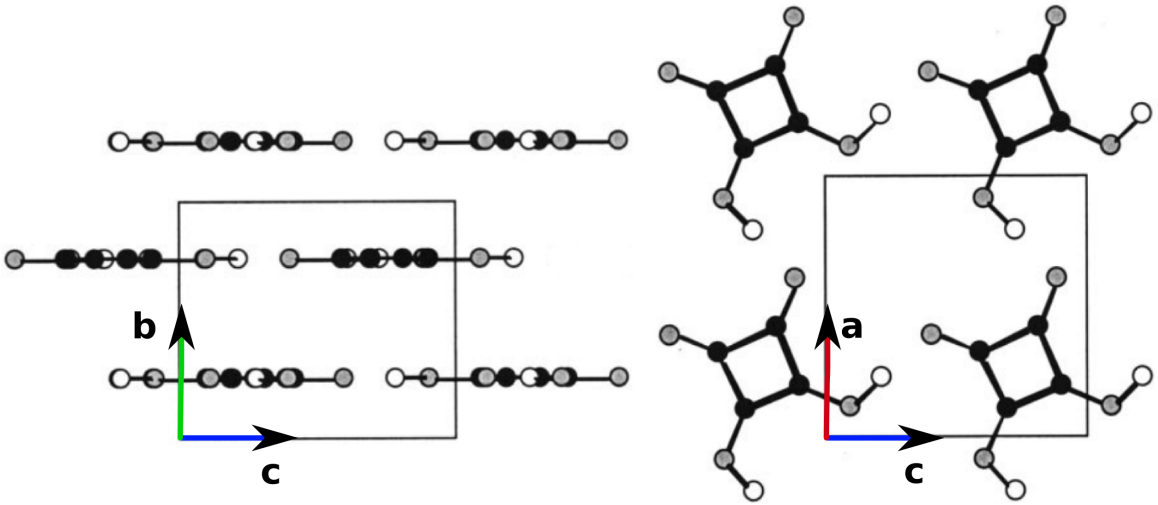


- thermal corrections needed for equilibrium structure and lattice energy[11]
- error compensation between missing dispersion and BSSE is not reliable
- identified by Computational Chemistry Highlights:
  "Most striking is the roughly 'MP2-quality' (...) obtained for non-covalent complexes and equilibrium structures (...) for medium-sized organic molecules."

more benchmark data on poster **P39** by **Eike Caldeweyher**

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

Squaric acid: simple crystal with interesting properties



Experimental interest

- dibutylester has medical applications in skin treatments[12]
- reagent for chemical synthesis

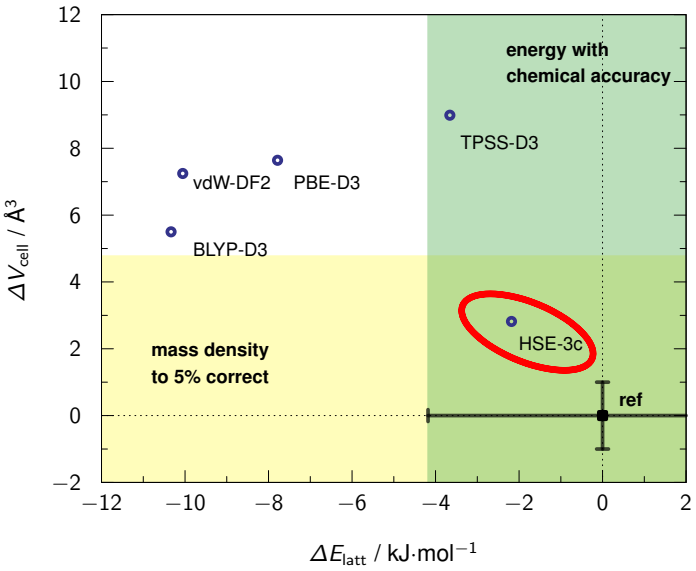
Theoretical challenge

- strong hydrogen bonds within and vdW stacking between layers
- phase transition from antiferro- to paraelectric[13]

[12] A. M. Holzer, W. R. Kaplan, *J. Drugs. Dermatol.*, **5**, 410 (2006)

[13] K. T. Wikfeldt, A. Michaelides, *J. Chem. Phys.*, **140**, 041103 (2014)

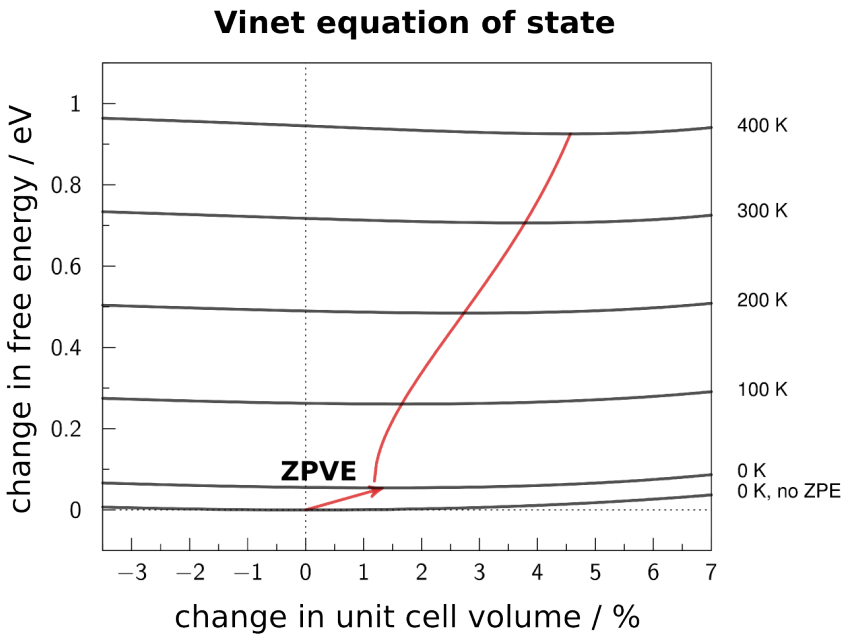
Hybrid functional needed for accurate description

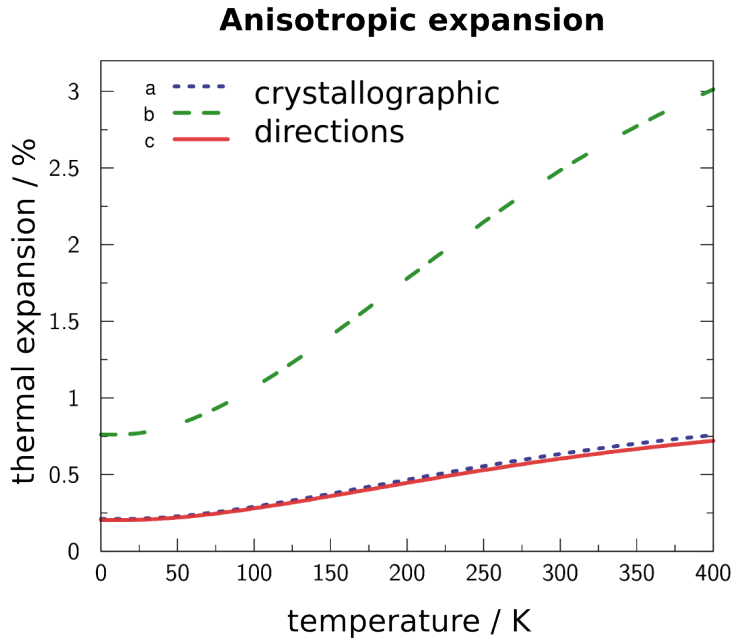


- GGAs are problematic, independent of dispersion correction
- HSE-3c provides both excellent energies and geometries
- low-temperature neutron scattering and sublimation measurements used for comparison

→ HSE-3c phonon modes with dense Brillouin zone sampling for quasi-harmonic treatment feasible

Quasi-harmonic treatment reveals strong anisotropic expansion



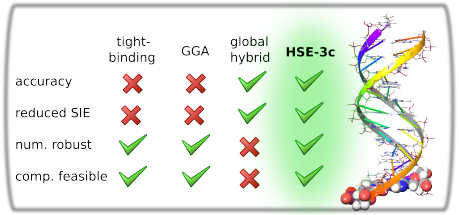


- substantial zero-point effect on unit cell
- predicted expansion in good agreement with new temperature dependent neutron scattering measurements[14]

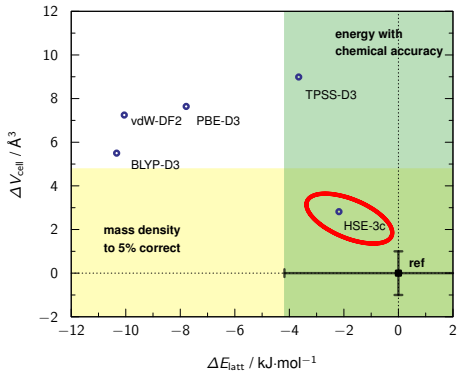
[14] in preparation

Summary

Conclusions

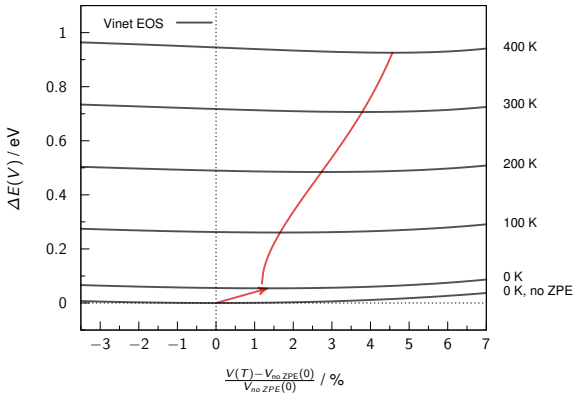


- cost-efficient method for routine electronic structure calculations needed
- HSE-3c is a promising new composite scheme
- quasi-harmonic treatment captures anisotropic thermal expansion



Outlook and possible improvements

- methods will be available in CRYSTAL17
- apply HSE-3c in the crystal structure prediction framework



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)

Funding

Alexander von Humboldt Stiftung/Foundation

813 dfg·sfb
Chemie an Spinzentren
SFB 813 der Deutschen
Forschungsgemeinschaft

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