

# A new screened exchange hybrid functional:

## Accurate and efficient structures and interaction energies

Dr. Jan Gerit Brandenburg<sup>1,2</sup>

<sup>1</sup>London Centre for Nanotechnology, Department of Chemistry, University College London, UK

<sup>2</sup>Mulliken Center for Theoretical Chemistry, University of Bonn, Germany



### Abstract

A highly efficient new composite scheme **HSE-3c** is proposed. We use the efficiency of medium sized Gaussian orbital expansions and the numerically robust screened exchange treatment based on the Henderson-Janesko-Skuseria (HJS) exchange hole model. This modified HSE functional is combined with semi-classical corrections for London dispersion and basis set deficiencies boosting its accuracy to 'MP2 quality' with a tiny fraction of the computational cost. In particular the description of systems with metallic characteristics is numerically robust, which leads to additional speed ups of ~50% compared to global hybrids in the same basis set.

### Electronic structure of large (periodic) systems

#### Target systems

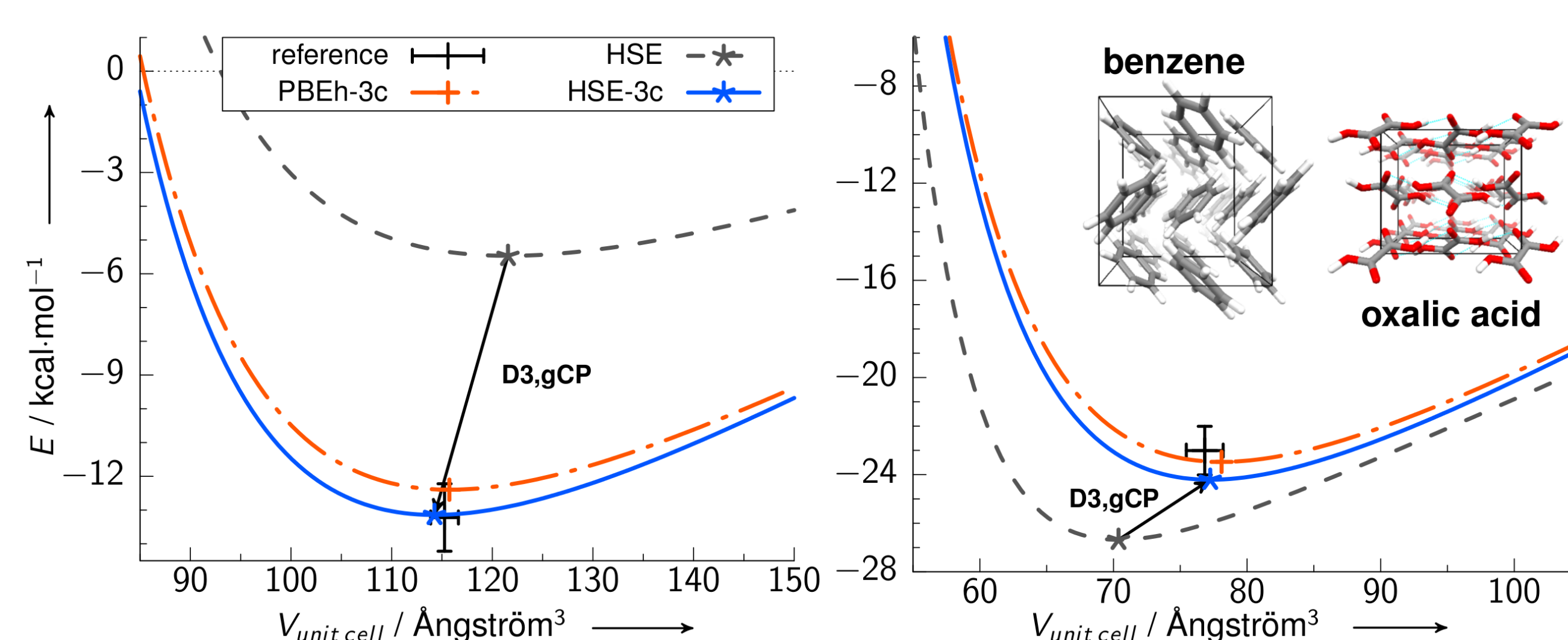
- protein structures and deoxyribonucleic acid
- metal-organic frameworks and organic semi-conductors
- metallic characteristic leads to small orbital energy gap



→ need for an efficient and robust hybrid density functional<sup>[1]</sup>

### Benchmarking of the new method

#### Potential energy surface of two representative organic crystals

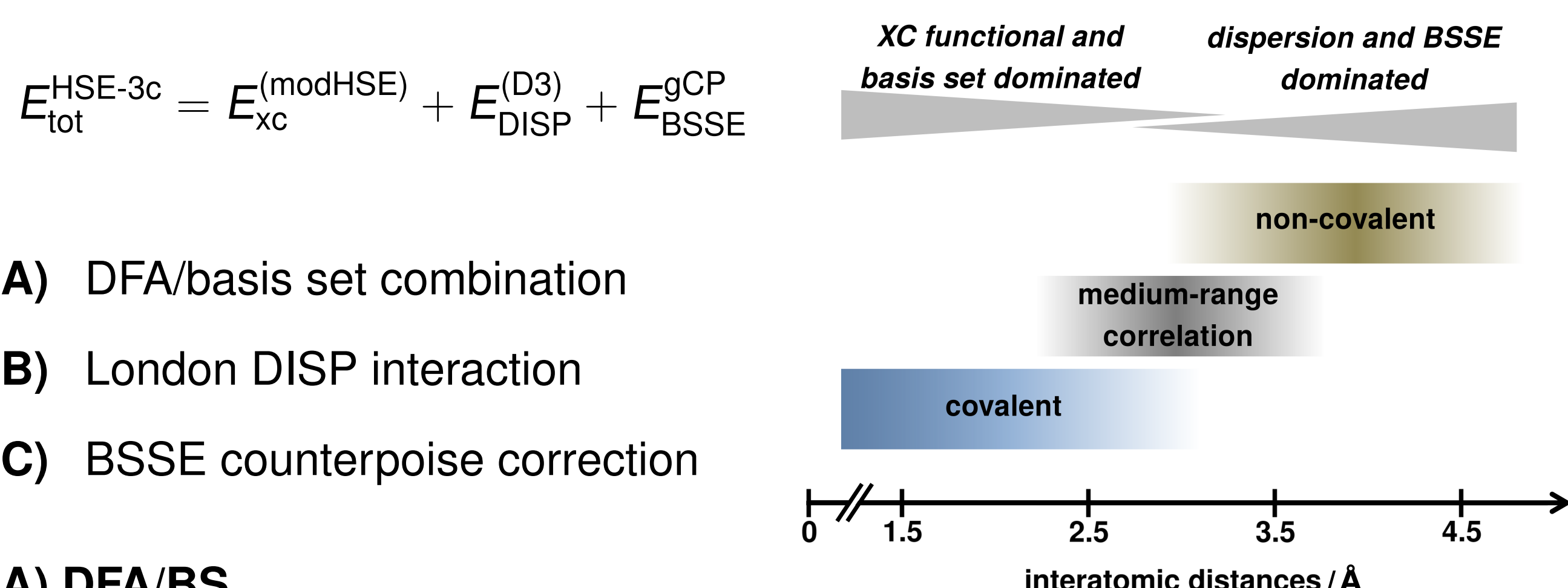


Identified by Computational Chemistry Highlights:

**“Most striking is the roughly ‘MP2-quality’ (...) obtained for non-covalent complexes and equilibrium structures (...) for medium-sized organic molecules.”**

### Design principles of HSE-3c

#### Ingredients for density functional construction



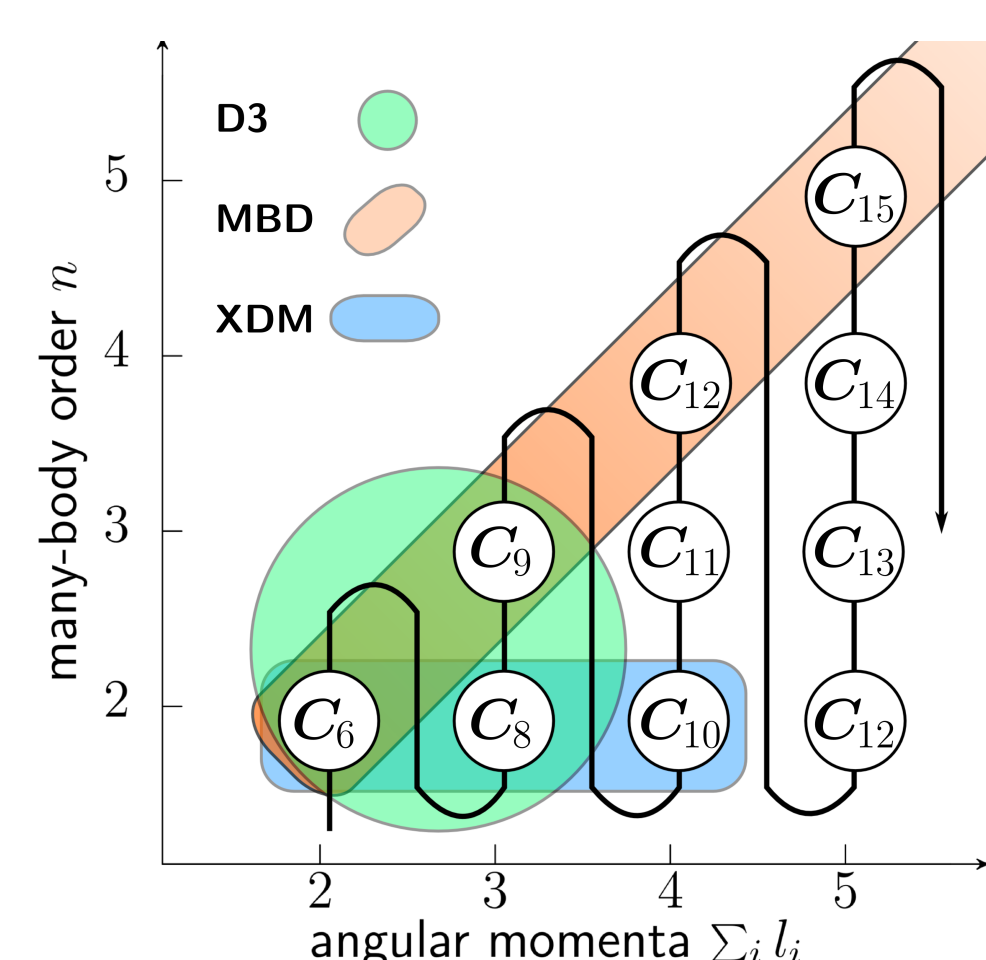
- (A) DFA/basis set combination
- (B) London DISP interaction
- (C) BSSE counterpoise correction

#### (A) DFA/BS

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

- screened exchange based on HJS hole model<sup>[2]</sup>
- large portion of SR Fock exchange reduces SIE
- efficient double- $\zeta$  GTO basis set def2-mSVP<sup>[3]</sup>

#### (B,C) D3 London DISP and gCP BSSE correction



$$\lim_{r_{\alpha\beta} \rightarrow \infty} E_{\text{c}}^{\alpha\beta} = -\frac{3}{\pi} \int_0^\infty \alpha^\alpha(i\omega) \alpha^\beta(i\omega) d\omega \times \frac{1}{r_{\alpha\beta}^6}$$

- $C_6$  from Casimir-Polder integration of TD-DFT excitations on model hydrides
- residual long-range error < 5%<sup>[4]</sup>
- gCP pair-potential generated from BS incompleteness measure

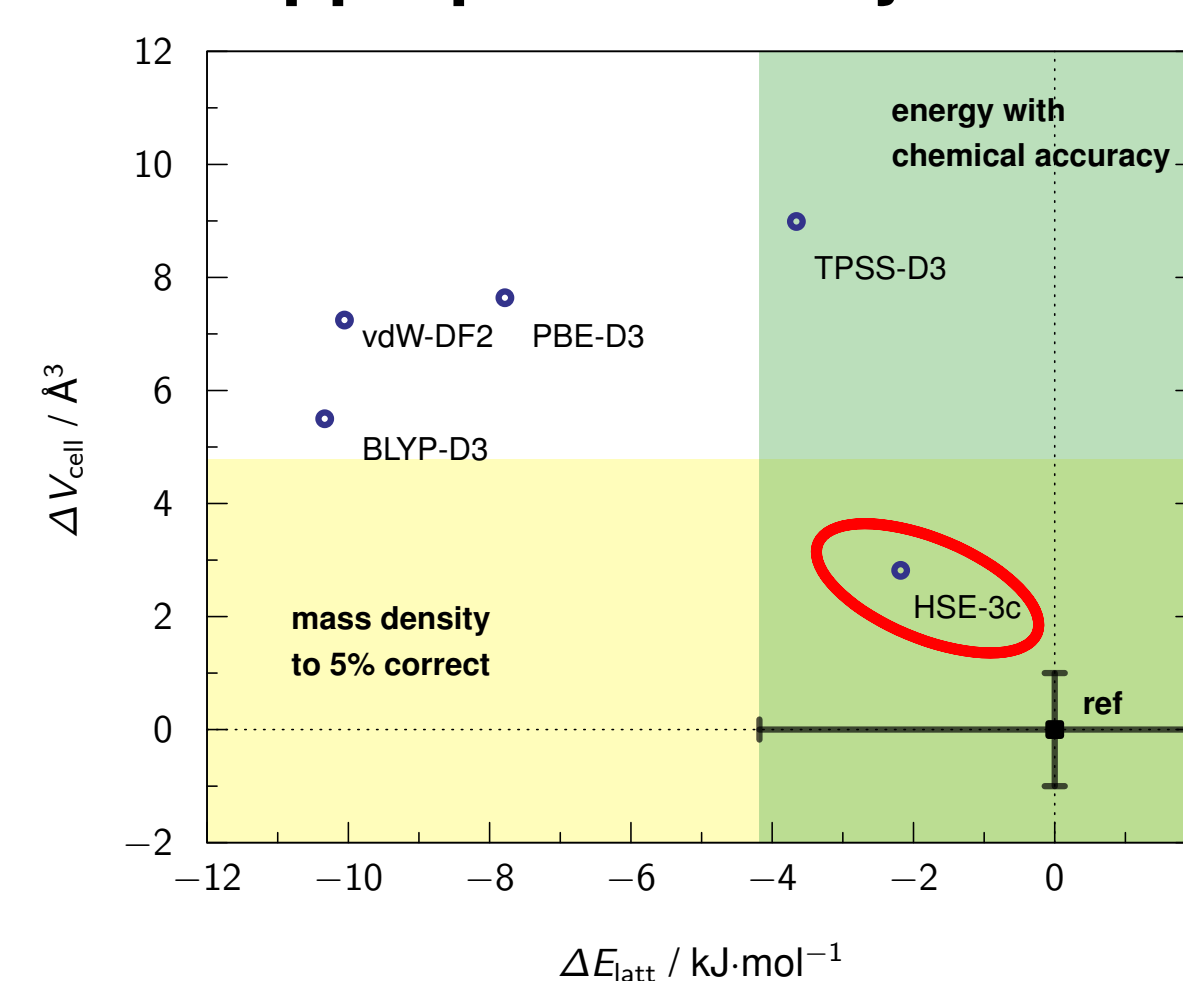
→ Implemented in CRYSTAL program package

### Thermal expansion of squaric acid

#### Interest of theoreticians and experimentalists

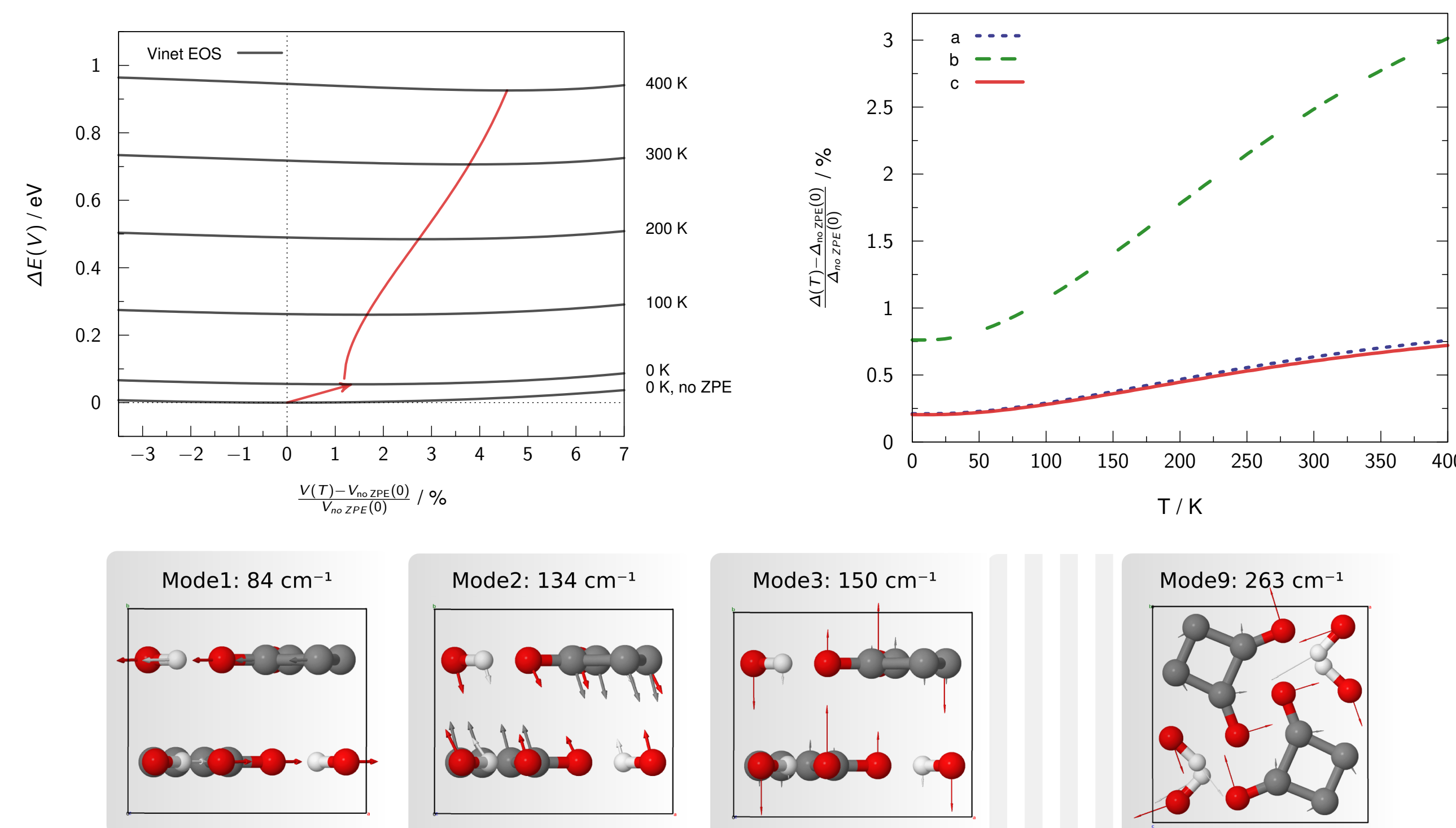
- uses in synthesis and medical applications
- strong hydrogen bonds within layers and vdW stacking between layers
- phase transition from ferro- to paramagnetic<sup>[5,6]</sup>

#### Choose appropriate density functional



- GGAs are problematic, independent of dispersion correction
- HSE-3c provides both excellent energies and geometries
- phonon modes with dense Brillouin zone sampling for QH-treatment feasible

#### Quasi-harmonic treatment reveals strong anisotropic expansion<sup>[7]</sup>

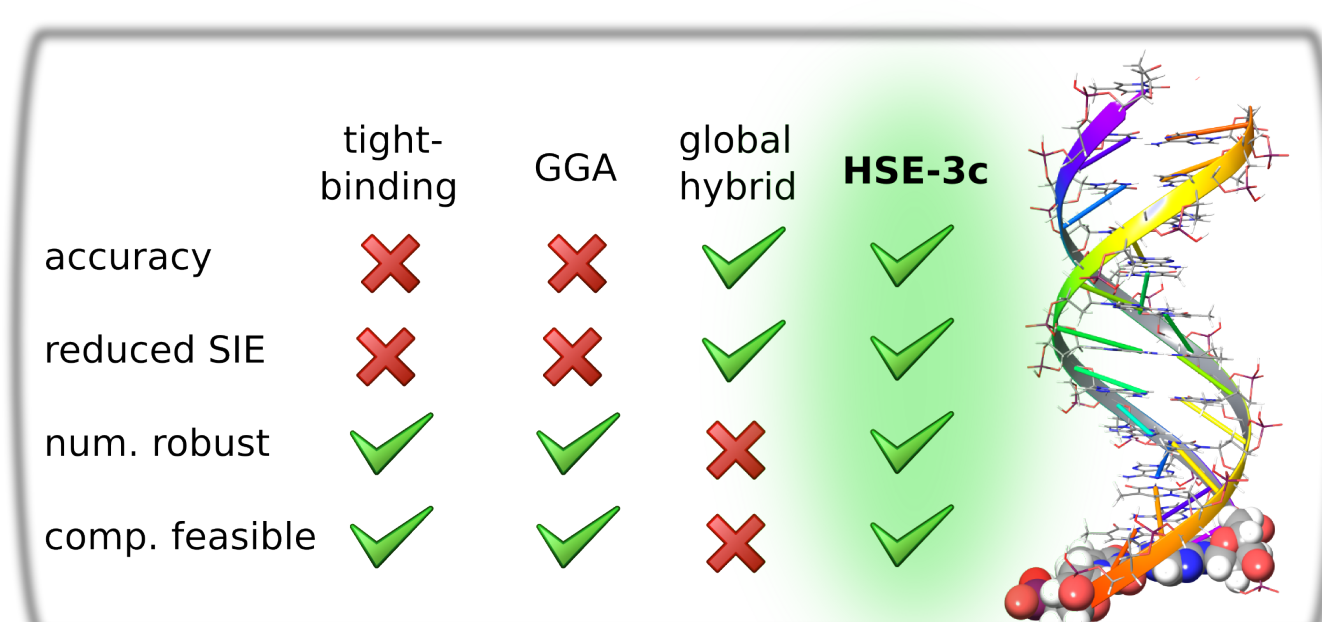


→ Predicted expansion in good agreement with new temperature dependent neutron scattering measurements

### DNA optimization on single Laptop computer

#### poly(dA) • poly(dT) double helix

- exploit rotational-translation symmetry within CRYSTAL
- small basis set increases speed substantially
- short-range Fock exchange reduces SIE



- [1] JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.* 18, 15519 (2016).
- [2] T. Henderson, B. Janesko, G. E. Scuseria, *J. Chem. Phys.* 128, 194105 (2008).
- [3] S. Grimme, JGB, A. Hansen, C. Bannwarth, *J. Chem. Phys.* 143, 54107 (2015).
- [4] S. Grimme, A. Hansen, JGB, C. Bannwarth, *Chem. Rev.* 126, 5105 (2016).
- [6] K. T. Wikfeldt, A. Michaelides, *J. Chem. Phys.* 140, 041103 (2014).
- [7] JGB, F. Fernandez-Alonso, S. L. Price, A. Michaelides, *in preparation*