



Van der Waals corrections in the DFT framework

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MSSC2020: AB INITIO MODELLING IN SOLID STATE CHEMISTRY - IMPERIAL COLLEGE LONDON

Outline of talk



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- 1 Introduction
- 2 H₂ model system
- 3 Adiabatic connection fluctuation dissipation theorem (ACFDT)
- 4 Van der Waals inclusive density functional approximations
- 5 Show-cases
- 6 Conclusions

Recommended literature



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- Anthony Stone, *The theory of forces*, 2nd ed.; Oxford University Press, Oxford (2013)
- I. Kaplan, *Intermolecular interactions*; Wiley (2006)
- S. Grimme, A. Hansen, J. G. Brandenburg, C. Bannwarth, *Dispersion-Corrected Mean-Field Electronic Structure Methods*, Chem. Rev., **116**, 5105 (2016)

Other review articles

- J. Klimeš, A. Michaelides, *Perspective: Advances and challenges in treating van der Waals dispersion forces in density functional theory*, J. Phys. Chem., **137**, 120901 (2012)
- J. Hoja, A. Reilly, A. Tkatchenko, *First-principles modeling of molecular crystals: structures and stabilities, temperature and pressure*, WIREs Comput. Mol. Sci., **7** (2017)

Understanding phenomena in nature



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How can a Gecko
stick to a glass wall?

- cannot be explained by classical mechanics
- London dispersion (C_6)



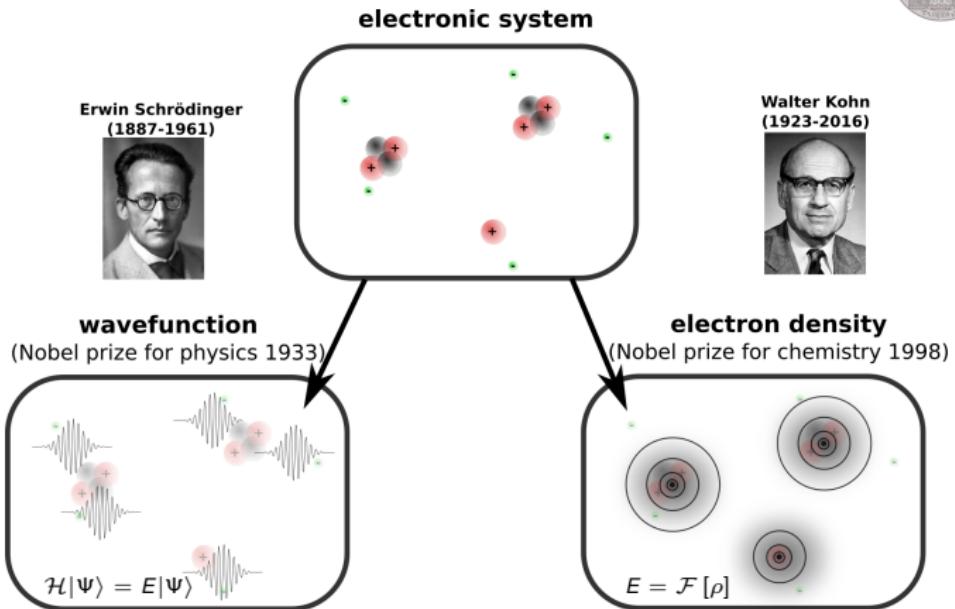
Why does a tablet change
its properties?

- van der Waals interaction stabilizes tablet dependent on its form
- relevant for production process and dosage

Possible theoretical ansatz



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- exact in principle
- complicated to solve
- semi-local, easier to solve
- **no London dispersion**

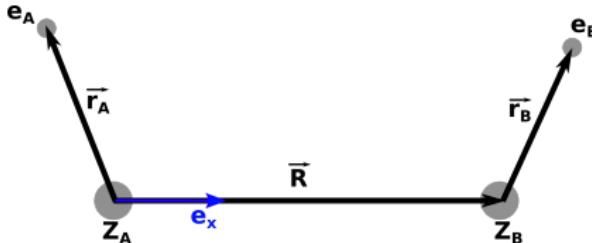
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Definition of the model system



- nuclei fixed, Hilbert space $\mathcal{H}_A = \mathcal{H}_B = \mathcal{L}^2(\mathbb{R}^d)$
- Hamiltonian $\hat{H} = \hat{H}_0^A + \hat{H}_0^B + \hat{H}_I$
- interaction $\hat{H}_I = \frac{1}{R} + \frac{1}{|\mathbf{R} - \mathbf{r}_A + \mathbf{r}_B|} + \frac{1}{|\mathbf{R} - \mathbf{r}_A|} + \frac{1}{|\mathbf{R} + \mathbf{r}_B|}$
- assume R large enough to ignore Fermionic symmetry
- specific form of $\hat{H}_0^{A/B}$ not relevant, only assume rotational symmetry, i.e.
 $[\hat{H}_0^{A/B}, \hat{U}] = 0$, and $\hat{U}|\Psi(\mathbf{r}_A, \mathbf{r}_B)\rangle = |\Psi(U\mathbf{r}_A, \mathbf{r}_B)\rangle$
rotation matrix U (± 1 for one dimension)

Second order perturbation theory



- expand \hat{H}_I in powers of $1/R$:

$$\hat{H}_I = \frac{(\mathbf{r}_A \mathbf{r}_B) R^2 - 3(\mathbf{r}_A \mathbf{R})(\mathbf{r}_B \mathbf{R})}{R^5} = \frac{\mathbf{r}_A \mathbf{r}_B - 3x_A x_B}{R^3} + \mathcal{O}(R^{-4})$$

- zero order ground state from direct product $|0\rangle = |0_A\rangle|0_B\rangle$
- rotational symmetry $\langle 0_A | \mathbf{r}_A | 0_A \rangle = 0$
- zero order energy

$$E_0^0 = \langle 0 | \hat{H}_0 | 0 \rangle = E_0^A + E_0^B$$

- first order energy

$$\begin{aligned} E_0^1 &= \langle 0 | \hat{H}_I | 0 \rangle \\ &= \langle 0 | \frac{1}{R^3} (\mathbf{r}_A \mathbf{r}_B - 3x_A x_B) | 0 \rangle + \mathcal{O}(R^{-4}) = 0 + \mathcal{O}(R^{-4}) \end{aligned}$$

Second order perturbation theory



- second order energy

$$\begin{aligned} E_0^2 &= - \sum_n' \frac{|\langle n | \hat{H}_I | 0 \rangle|^2}{E_n - E_0} \\ &= - \frac{1}{R^6} \sum_n' \frac{|\langle n | \mathbf{r}_A \mathbf{r}_B - 3\mathbf{x}_A \mathbf{x}_B | 0 \rangle|^2}{E_n - E_0} + \mathcal{O}(R^{-8}) \\ &= - \frac{1}{R^6} \sum_{n_A}' \sum_{n_B}' \frac{|\langle n_A n_B | \mu_A \mu_B | 0_A 0_B \rangle|^2}{E_n^A - E_0^A + E_n^B - E_0^B} + \mathcal{O}(R^{-8}) \\ &= - \frac{6}{R^6} \sum_{n_A}' \sum_{n_B}' \frac{1}{\omega_{0n}^A + \omega_{0n}^B} (|\langle n_A | \mu_A | 0_A \rangle|^2 |\langle n_B | \mu_B | 0_B \rangle|^2) + \mathcal{O}(R^{-8}) \end{aligned}$$

- excitation energies $\omega_{0n}^A = E_n^A - E_0^A$, spherical dipole operators μ_A
- MacLachlan integral identity $\frac{1}{A+B} = \frac{2}{\pi} \int d\omega \frac{AB}{(A^2+\omega^2)(B^2+\omega^2)}$

Second order perturbation theory



- second order energy

$$\begin{aligned} E_0^2 &= -\frac{1}{R^6} \frac{3}{\pi} \int d\omega \left[\sum_{n_A} \frac{\omega_{0n}^A |\langle n_A | \mu_A | 0_A \rangle|^2}{\omega_{0n}^A - (i\omega)^2} \right] \left[\sum_{n_B} \frac{\omega_{0n}^B |\langle n_B | \mu_B | 0_B \rangle|^2}{\omega_{0n}^B - (i\omega)^2} \right] \\ &= -\frac{1}{R^6} \frac{3}{\pi} \int d\omega \alpha^A(i\omega) \alpha^B(i\omega) \end{aligned}$$

- dynamical dipole polarizabilities $\alpha^{A/B}$
- dispersion coefficients $C_6^{AB} = \frac{3}{\pi} \int d\omega \alpha^A(i\omega) \alpha^B(i\omega)$
- well known expression for London dispersion energy

$$E_0^2 = -\frac{C_6^{AB}}{R^6}$$

Absence of $1/R^7$ terms



- inversion operator: $\hat{I}|\Psi(\mathbf{r}_A, \mathbf{r}_B)\rangle = |\Psi(-\mathbf{r}_A, -\mathbf{r}_B)\rangle$
- \hat{I} is symmetry of system: $[\hat{I}, \hat{H}] = 0$
- $|n\rangle$ are eigenstates of \hat{I} , $\hat{I}^2 = 1$, $\hat{I}\mathbf{r}_A\hat{I} = -\mathbf{r}_A$
- split perturbation sum

$$\begin{aligned} E_0^2 &= - \sum_n, \frac{|\langle n | \hat{H}_I | 0 \rangle|^2}{E_n - E_0} \\ &= - \sum_{\substack{n \\ \hat{I}|n\rangle=+|n\rangle}} , \frac{|\langle n | \hat{H}_I | 0 \rangle|^2}{E_n - E_0} - \sum_{\substack{n \\ \hat{I}|n\rangle=-|n\rangle}} , \frac{|\langle n | \hat{H}_I | 0 \rangle|^2}{E_n - E_0} \end{aligned}$$

- no mixed terms of even and uneven power of R possible
→ no R^{-7} term in second order expansion

Consistency of perturbation expansion



- for consistency, higher order expansion of \hat{H}_I in first order energy needed
- straight-forward expansion in *Am. J. Phys.* **83**, 150 (2015), App. B
- rewrite first order energy

$$\begin{aligned}E_0^1 &= \langle 0 | \hat{H}_I | 0 \rangle = \langle 0_B | V_A(\mathbf{R}) - V_A(\mathbf{R} + \mathbf{r}_B) | 0_B \rangle \\V_A(\mathbf{r}) &= \langle 0_A | \frac{1}{r} - \frac{1}{|\mathbf{r} - \mathbf{r}_A|} | 0_A \rangle \\&= \langle 0_A | -\frac{\mathbf{r}\mathbf{r}_A}{r^3} + \frac{r_A^2}{2r^3} - \frac{3(\mathbf{r}\mathbf{r}_A)^2}{2r^5} + \mathcal{O}(r^{-4}) | 0_A \rangle\end{aligned}$$

- employ identity $\langle 0_A | |\mathbf{r}_A|^2 | 0_A \rangle |\mathbf{r}|^2 = d \langle 0_A | |\mathbf{r}\mathbf{r}_A|^2 | 0_A \rangle$
- characteristic length $a^2 = \frac{\langle 0_A | |\mathbf{r}_A|^2 | 0_A \rangle}{d}$

Consistency of perturbation expansion



- first order energy

$$E_0^1 = \frac{3(3-d)(5-d)a^2}{4} \frac{1}{R^5} + \mathcal{O}(R^{-7})$$

- for $d = 3$, first order term vanishes and attractive R^{-6} is the leading order
- for $d = 1, 2$, E_0^1 is nonzero and repulsive R^{-5} is the leading order

Summary: H₂ model

- leading order energy: attractive R^{-6} in 3D and repulsive R^{-5} in 1D/2D
- C_6 dispersion coefficients can be computed from dynamical polarizabilities of separated atoms

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Exact expression for correlation energy from response function



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

- from adiabatic connection fluctuation dissipation theorem^[1]
- Coulomb interaction scaled by λ
- linear response of the electron density with respect to local perturbation

$$\delta\rho(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', i\omega) \delta V^{\text{ext}}(\mathbf{r}', \omega)$$

- relation to dynamic polarizability

$$\alpha_{ij}(i\omega) = \int d\mathbf{r} d\mathbf{r}' r_i r_j' \chi(\mathbf{r}, \mathbf{r}', i\omega)$$

^[1] A. Zangwill, P. Soven, *Phys. Rev. A* **21**, 1561 (1980)

In practice not solvable for many-particle systems



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

- analytical expression for non-interaction Kohn-Sham system

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

- occupied and virtual KS orbitals φ_i and φ_a
- χ_λ too complicated to compute in practice
→ approximation needed

[¹] A. Zangwill, P. Soven, *Phys. Rev. A* **21**, 1561 (1980)

Coarse-graining to atomic contributions leads to significant simplifications



- coarse-grain ACFDT to fragment contributions

$$E_{\text{disp}}^{AB} = -\frac{1}{2\pi} \int d\omega \int d\mathbf{r}_a d\mathbf{r}'_a d\mathbf{r}_b d\mathbf{r}'_b \frac{\chi(\mathbf{r}_a, \mathbf{r}'_a, i\omega) \chi(\mathbf{r}_b, \mathbf{r}'_b, i\omega)}{|\mathbf{r}_a - \mathbf{r}'_a| |\mathbf{r}_b - \mathbf{r}'_b|}$$

- assume vanishing overlap to factorize response function
- integrate fragment response to dynamic polarizabilities

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

- expansion of Coulomb operator in multipoles

$$E_{\text{disp}}^{AB} = -\frac{2}{\pi} \sum_{\substack{\alpha, \beta \\ \gamma, \delta}} \left(\nabla_\alpha \nabla_\beta \frac{1}{R} \right) \left(\nabla_\gamma \nabla_\delta \frac{1}{R} \right) \int d\omega \alpha_{\alpha\beta}^A(i\omega) \alpha_{\gamma\delta}^B(i\omega)$$

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

Spherical averaging and higher order terms beyond dipole-dipole



- spherical averaging of dyn. polarizabilities

$$E_{\text{disp}}^{AB} = - \underbrace{\frac{3}{\pi} \int d\omega \alpha_A(i\omega) \alpha_B(i\omega)}_{C_6^{AB}} \times \frac{1}{R_{AB}^6} + \mathcal{O}(R^{-8})$$

- beyond dipole terms from higher multipole expansion, e.g. C_8 dipole-quadrupole, C_{10} quadrupole-quadrupole, etc

$$E_{\text{disp}}^{AB} = - \frac{C_6^{AB}}{R_{AB}^6} - \frac{C_8^{AB}}{R_{AB}^8} - \frac{C_{10}^{AB}}{R_{AB}^{10}} + \mathcal{O}(R^{-12})$$

- beyond pair-wise terms from multi-fragment terms, e.g C_9 dipole-dipole-dipole

$$C_9^{ABC} = - \frac{3}{\pi} \int d\omega \alpha_A(i\omega) \alpha_B(i\omega) \alpha_C(i\omega)$$

Combining vdW correction with mean field model

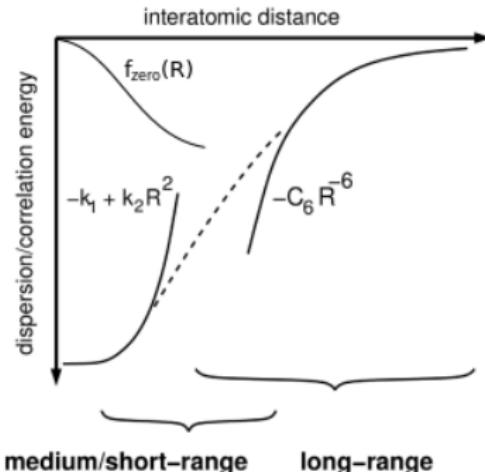


- sum of fragment contributions for total London dispersion energy

$$E_{\text{disp}} = -\frac{1}{2} \sum_{A,B}^{\text{pairs}} \sum_n \frac{C_n^{AB}}{R_{AB}^n} - \frac{1}{6} \sum_{A,B,C}^{\text{triples}} \sum_n \frac{C_n^{ABC}}{R_{ABC}^n} F^{\text{geom}} + \mathcal{O}(\text{quadruples})$$

- singularity at short-range (and expansion not valid)
- introduce short-range damping, motivated by range separation of Coulomb operator

$$E_{\text{tot}}^{AB} = E_{\text{DFT}}^{AB} \text{erf}(\omega R_{AB}) + E_{\text{disp}}^{AB} \text{erfc}(\omega R_{AB})$$



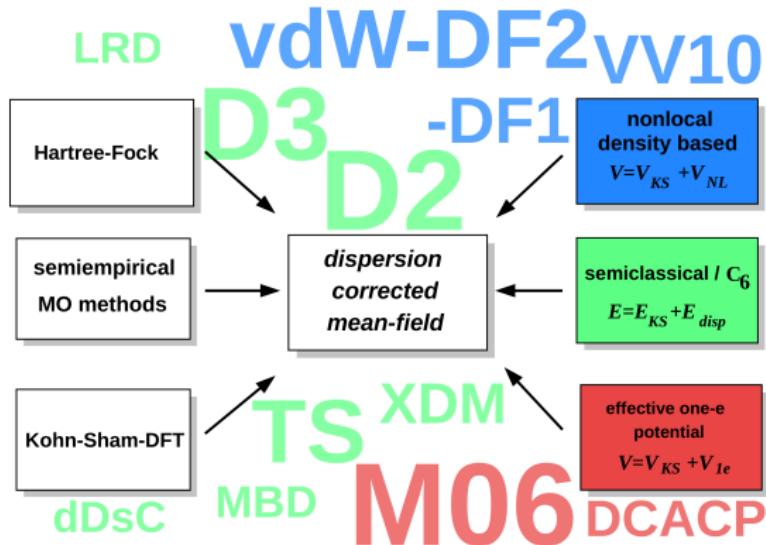
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Many good dispersion corrections exist



- focus on D3 scheme as it can be used at all computational levels
- own work started with extension of D3 type corrections

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

Coarse-graining to atomic contributions leads to significant simplifications



- coarse-grain to atomic contributions

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

- expansion of Coulomb operator in multipoles^[5]

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

- C_8^{AB} and C_9^{AB} from recursion relations and averages^[4]

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

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

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

Dynamic polarizability via linear response DFT



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- use frequency domain formalism to get excitation frequencies^[5]

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{A}^* & \mathbf{B}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

- orbital rotation matrices

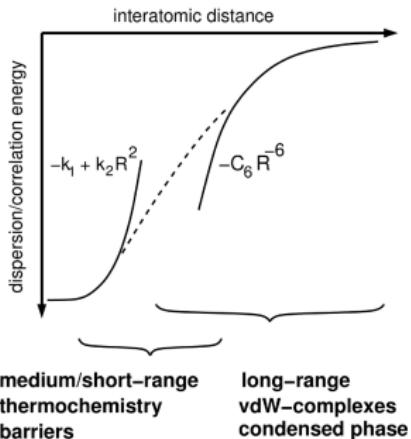
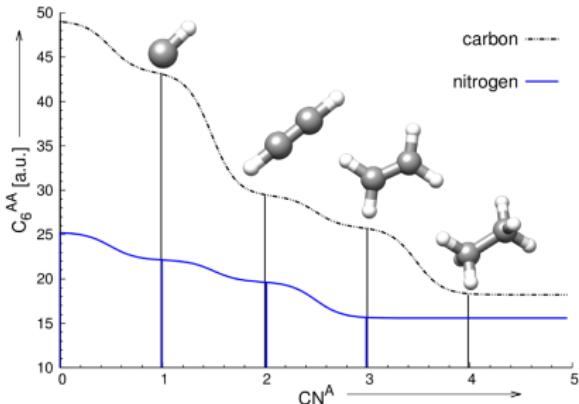
$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \langle ab | 1/r | ij \rangle + \langle ab | f_{xc} | ij \rangle$$

$$B_{ia,jb} = \langle aj | 1/r | ib \rangle + \langle aj | f_{xc} | ib \rangle$$

- approximation: neglect frequency dependence of f_{xc} and use ground state functional (PBE38)
- similar to random phase approximation with exchange

^[5] M. E. Casida, *Recent Advances in Density Functional Methods*, D. P. Chong (World Scientific, Singapore), 155 (1995)

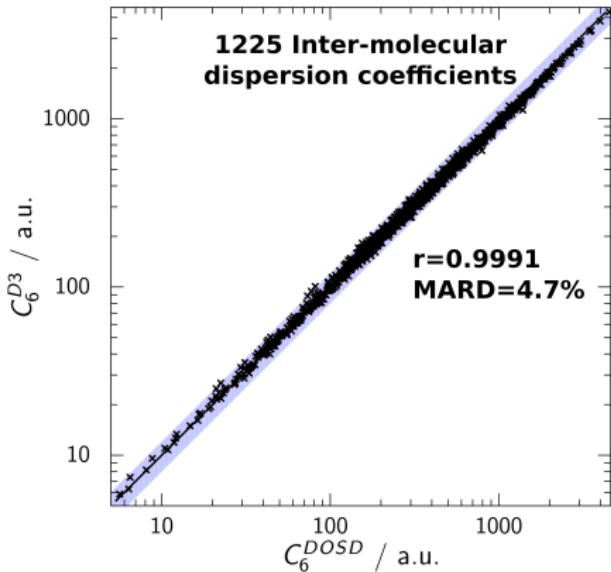
Geometric coordination number for interpolations of reference C_6



- 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^[6]

[6] 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 (DOSD) yield $C_6^{\text{exptl.}}$ (compiled by A. Tkatchenko)
- residual long-range mean absolute relative deviation (MARD) of D3 < 5% [7]
- deviations are close to intrinsic TD-DFT errors of $\alpha(i\omega)$

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

D3 in a nutshell: High accuracy at force field speed



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Advantages of D3 model

- intermolecular C_6 coefficients are very accurate
- no electronic structure input needed
- computation is extremely fast
 $D3(\text{two-body}) \sim \text{FF speed}$
- analytical first (and second) derivatives

Possible shortcomings

- no automatic adjustment to unusual electronic structures^[*]
- missing anisotropy of dispersion interaction
- no many-body contributions beyond Axilrod-Teller-Muto term
- high empiricism in short-range damping

Simple input of D3 dispersion correction in CRYSTAL17



old calculation

```
MOLECULE
40
2
6 1.209708 0.698426 0.000000
1 2.152747 1.242889 0.000000
BASISSET
def2-mTZVP
DFT
PBE
END
END
```

new D3 inclusive calculation

```
MOLECULE
40
2
6 1.209708 0.698426 0.000000
1 2.152747 1.242889 0.000000
BASISSET
def2-mTZVP
DFT
PBE-D3
END
END
```

***** DFT-D3 DISPERSION ENERGY CORRECTION

```
D3 DISPERSION ENERGY (AU)      -1.0948042757474E-02
TOTAL ENERGY + DISP (AU)       -2.3201130812713E+02
```

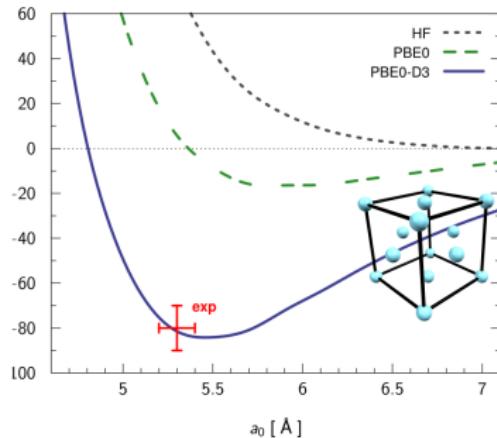
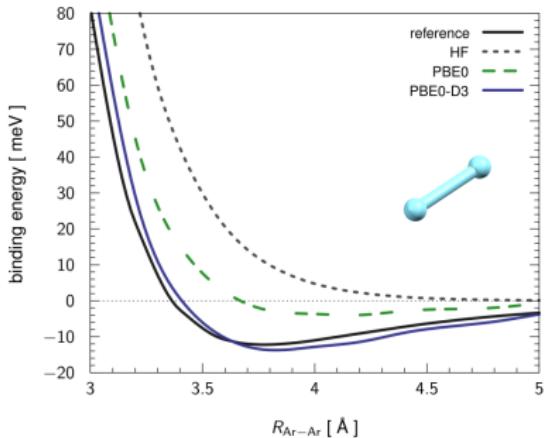
- combinable with geometry optimization, frequencies, QHA, etc.
- impact of D3 should be tested for all DFT applications

Guinea pig for testing vdW interactions



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Noble gas assemblies

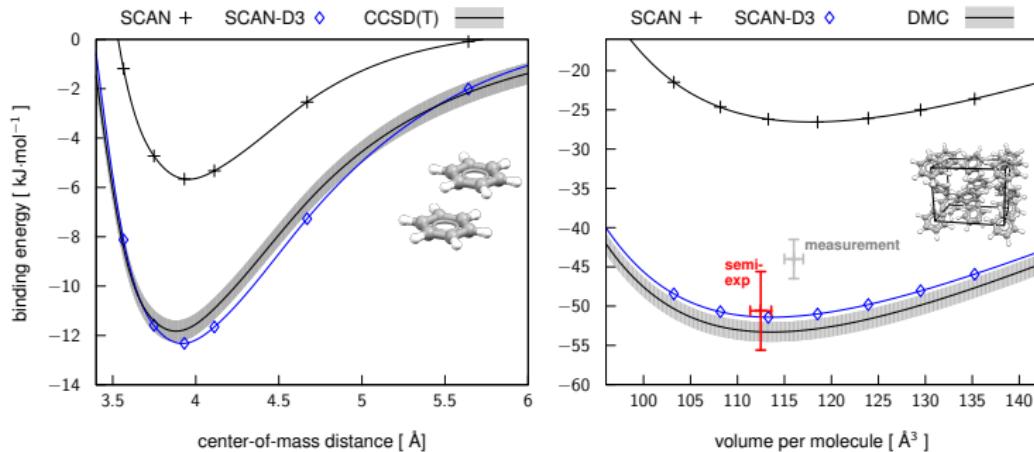


- binding solely from electron correlation effects

Guinea pig for testing vdW interactions



Benzene dimer and crystal



- zero-point and thermal effects crucial for comparing to measurement
- error bar in volume mainly from QHA back-correction (about 1%)

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Numerical convergence & different functional approximations



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- check literature if similar systems have been studied
- are high-level theory data available?
→ use those or generate your own
- are experimental references available?
→ be careful to compare the right observables
- converge all numerical thresholds
(basis set, k -point sampling, SCF/geometry thresholds)
- different methods in terms of computational efficiency and accuracy
→ influence of XC treatment (PBE vs. BLYP vs. SCAN vs. PBE0)
→ vdW correction should always be included (D3, MBD, XDM, vdW-DF2)
- use affordable method with acceptable accuracy

if none exist abandon project

Multilevel methodologies: Finding the right compromise



	task/property	example method
accurate QM	single-point energy	many-body WFT (CCSD(T), DMC ^[8])
cheap QM	optimization	DFT ^[9,10] (HSE-3c ^[11])
very cheap QM	optimization/Hessians conformations	semi-empirical ^[12,13]
force field	dynamics conformational sampling	transferable or molecule specific (QM derived) FF

^[8] A. Zen, JGB, J. Klimeš, A. Tkatchenko, D. Alfè, A. Michaelides, *Proc. Natl. Acad. Sci. U.S.A.*, **115**, 1724 (2018).

^[9] JGB, J. E. Bates, J. Sun, J. P. Perdew *Phys. Rev. B*, **94**, 115144 (2016).

^[10] JGB, et al. *JCP*, **148**, 064104 (2018). ^[11] JGB, E. Caldeweyher, S. Grimme, *PCCP* **18**, 15519 (2016).

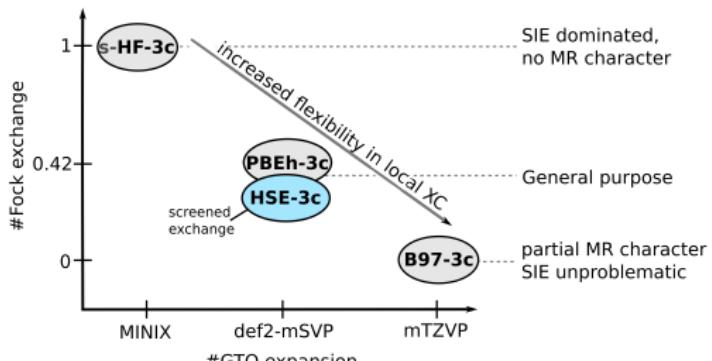
^[12] JGB, S. Grimme, *JPCL*, **5**, 1785 (2014). ^[13] M. Mortazavi, JGB, R. J. Maurer, A. Tkatchenko, *JPCL*, **9**, 399 (2018).

Full hierarchy of 'low-cost' methods



HSE-3c construction principles

- fast for optimizations and frequencies → compact orbital expansion
- avoid most self-interaction error → use Fock exchange
- numerically robust → screening of Fock exchange
- combine with semi-classical correction potentials (3c)

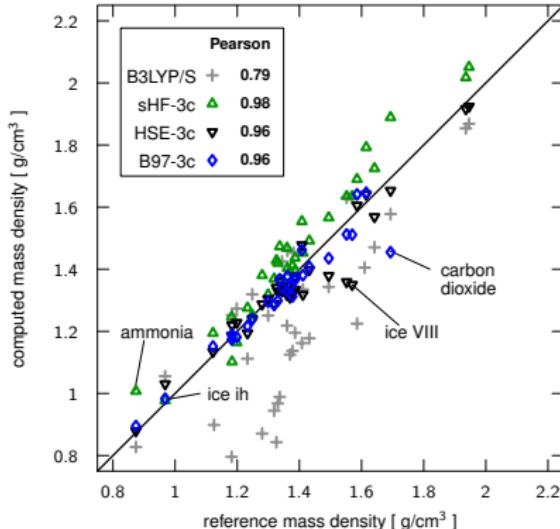
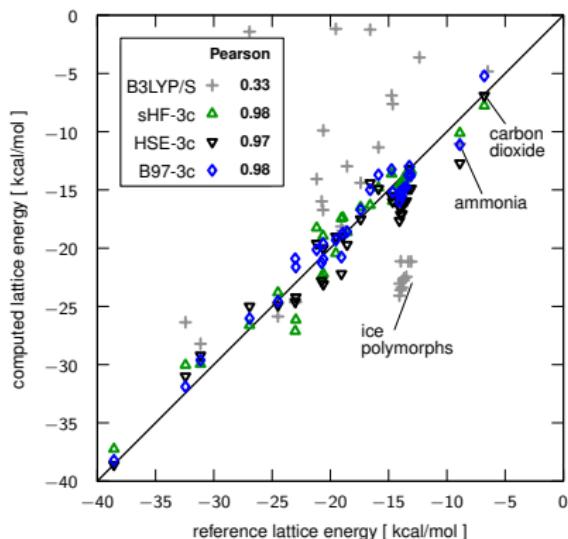


[¹⁴] E. Caldeweyher, JGB, J. Phys.: Condens. Matter **30**, 213001 (2018) [Psi-k Highlight Jan. 2019]

Good results on molecular crystals



X23^[15,16] and ICE10^[17] benchmark sets:

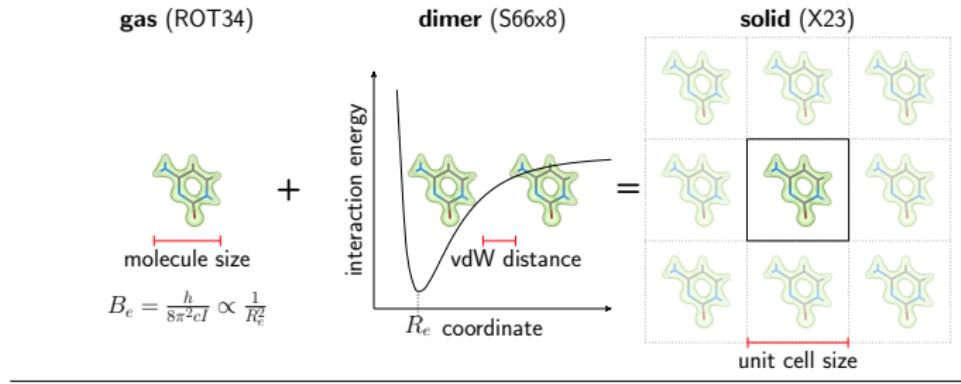


- consistent structures and interaction energies by HSE-3c

^[15] E. Johnson, A. Otero-de-la-Roza, *J. Chem. Phys.* **137**, 054103 (2012), ^[16] A. Reilly, A. Tkatchenko, *JCP* **139**, 024705 (2013)

^[17] JGB, T. Maas, S. Grimme, *J. Chem. Phys.* **142**, 124104 (2015)

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 %

Fast electronic structure with ab-initio accuracy

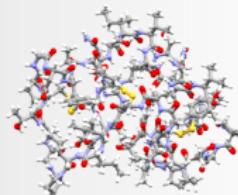


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gas phase protein

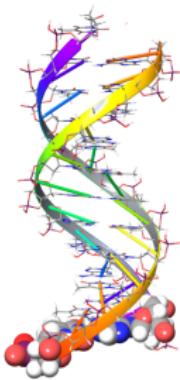
dim:
#atoms/unit:
wall time:
(HSE-3c on 16 cores)

0D
647 (647)
5h



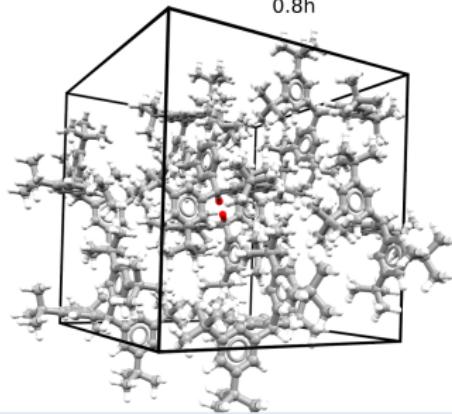
DNA helix

1D
726 (66)
0.5h



molecular crystal

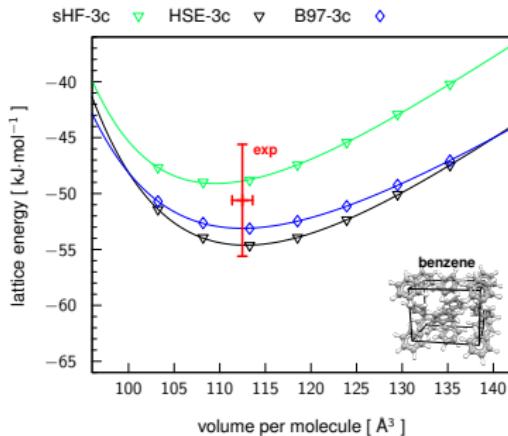
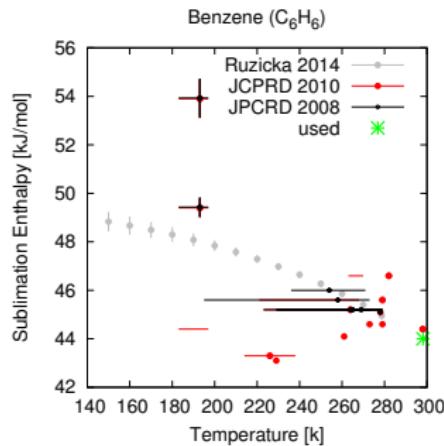
3D
856 (37)
0.8h



- fast computer code CRYSTAL17^[28] with cost-efficient methods
- enabling routine electronic structure calculation of large systems

^[18] R. Dovesi, A. Erba, R. Orlando, C. Zicovich-Wilson, B. Civalleri, L. Maschio, et al., *WIREs Comput. Mol. Sci.* **8**, 1360 (2018).

High-level QM data needed to test DFT for organic solids



- substantial uncertainties in $H_{\text{sub}}^{\text{exp}}$ and thermodynamic corrections [14]
- high-level data needed to judge approximate methods

[19] W. Acree, J. S. Chickos, *J. Phys. Chem. Ref. Data* 39, 043101 (2010).

Composite methods in CRYSTAL17

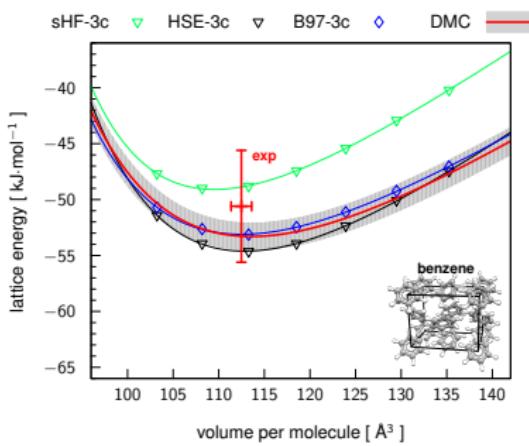
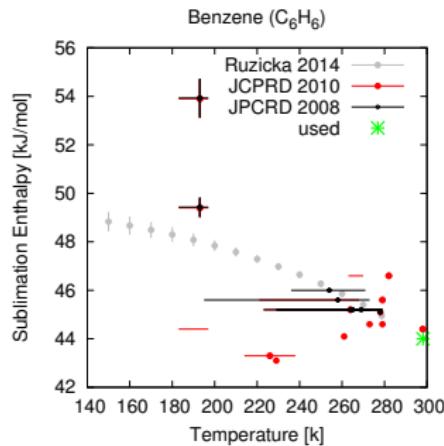


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```
CRYSTAL
0 0 0
61
    6.810      7.390      9.420
6
 6  0.00639   0.43997   0.35936 ! C
 6  0.87387   0.36203   0.45475 ! C
 6  0.13247   0.57749   0.40475 ! C
 1  0.01167   0.39362   0.24951 ! H
 1  0.77593   0.25368   0.42071 ! H
 1  0.23697   0.63726   0.33085 ! H
*****
BASISSET          DFT-D3-GCP DISPERSION AND COUNTERPOISE CORRECTION
def-mSVP
DFT
HSE-3c           D3 DISPERSION ENERGY (AU)      -8.1737930279612E-02
END              GCP ENERGY (AU)                 6.4006905922364E-02
SHRINK           TOTAL ENERGY + DISP + GCP (AU) -9.2702217782291E+02
4 4
END
*****
```

- consistent with geometry optimization, frequencies, QHA, etc.
- impact of D3 & BSSE should be tested for all DFT applications

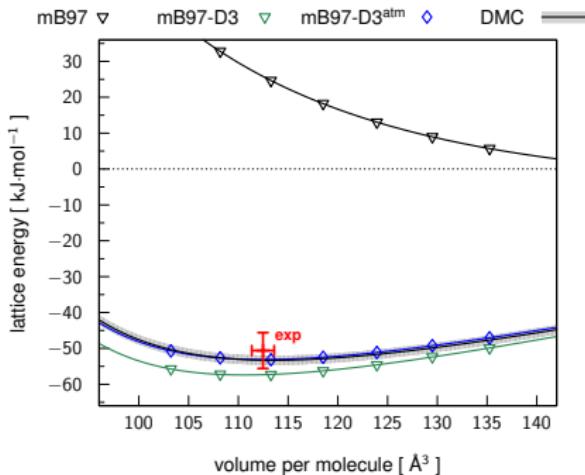
High-level QM data needed to test DFT for organic solids



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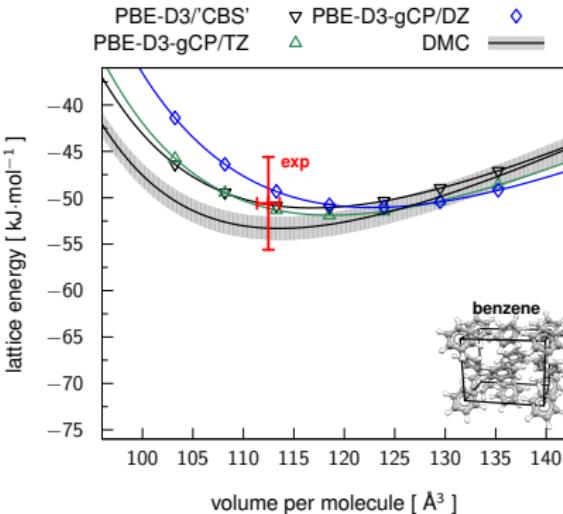
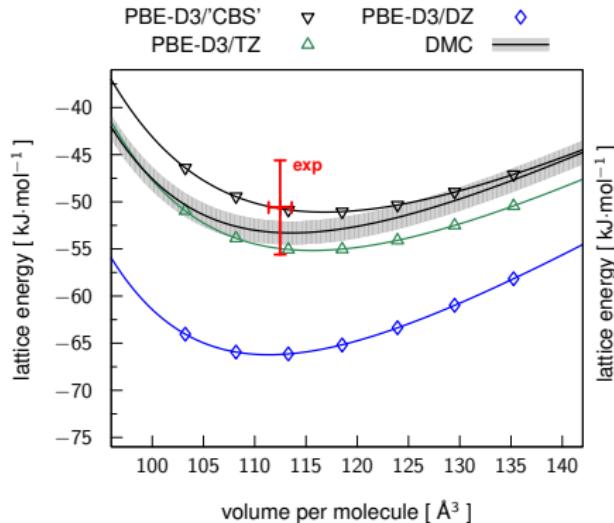
[19] W. Acree, J. S. Chickos, *J. Phys. Chem. Ref. Data* 39, 043101 (2010).

Modern DFT-D methods have excellent accuracy



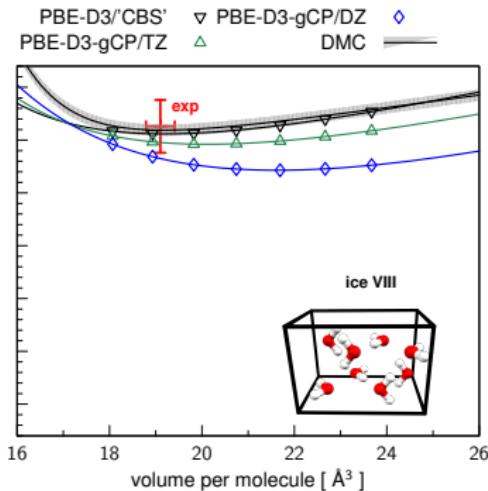
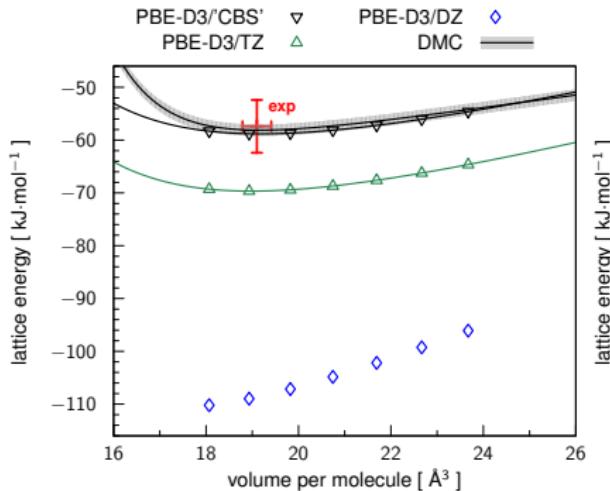
- benzene crystal purely vdW bonded
- significant effect of many-body dispersion

Choosing the right functional and basis set combination



- effect of semi-local functional as important as many-body dispersion
- significant BSSE up to triple- ζ basis sets

Choosing the right functional and basis set combination



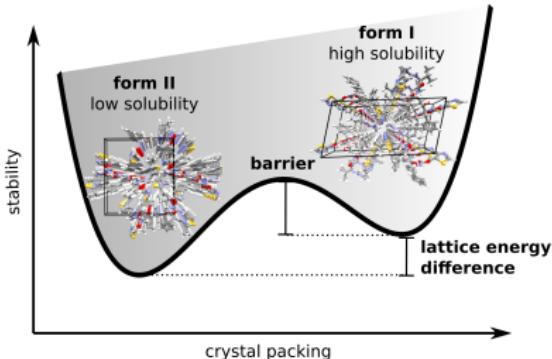
- ice VIII: high-density phase
- BSSE even stronger in H-bonded systems

Many properties depend on the polymorphic form of a crystal



Polymorphism

- ability of a molecule to crystallize in more than one structure^[20]
- properties change with crystal packing, e.g. solubility, color, etc.^[21]
- late appearing polymorph disrupted supply of antiviral drug ritonavir^[22]
 - Tools to predict possible polymorphs would be valuable
 - High accuracy $\sim 1 \text{ kJ/mol}$ needed



[20] A. J. Cruz-Cabeza, S. M. Reutzel-Edens, J. Bernstein, *Chem. Soc. Rev.* **44**, 8619-8635 (2015).

[21] S. L. Price, *JGB, Molecular Crystal Structure Prediction; Non-covalent interactions in Quantum Chemistry and Physics*, G. DiLabio, A. Otero-de-la-Roza, Eds., Elsevier Australia, Melbourne, ISBN: 9780128098356 (2017).

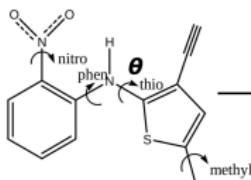
[17] J. Bauer, et al., *J. Pharm. Res.* **18**, 859-866 (2001).

Sampling and energetic ranking for crystal structure prediction



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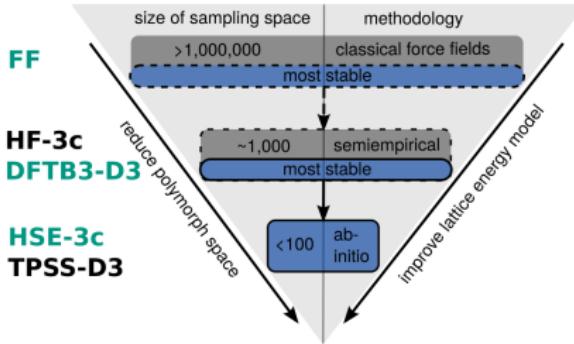
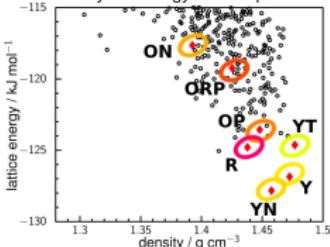
molecular diagram of ROY



CSP



crystal energy landscape



Properties
of ROY polymorphs
characterized

Red prism
 $P-1$, $\theta=21.7^\circ$

Orange Red Plate
 $Pbca$, $\theta=39.4^\circ$

Orange Needle
 $P2_1/c$, $\theta=52.6^\circ$

Yellow prism
 $P2_1/n$, $\theta=104.7^\circ$

uncharacterized



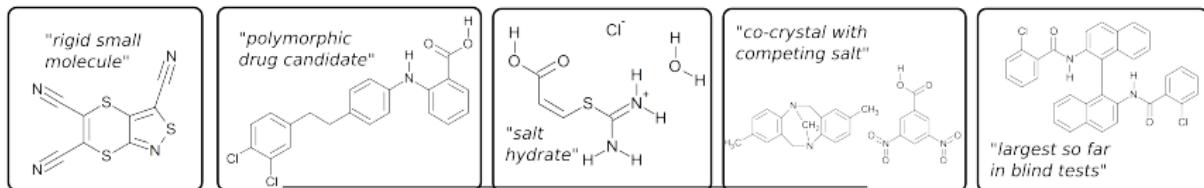
[23] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

[24] M. Vasileiadis, A. V. Kazantsev, P. G. Karamertzanis, C. S. Adjiman, C. C. Pantelides, *Acta Cryst. B* **68**, 677 (2012)

Promising results in the 6th blind test



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	22	23	24	25	26
PBE	2	1-9	6	3	1
PBE-D3	1	1-9	1	1	1
PBE-MBD	1	1-7	1	2	1
vdW-DF2	1	4-8	1	3	2
M06L	1	4-13	1	1	7

lattice energy on fixed TPSS-D3 structures

- good lattice energy based ranking of PBE-D3
- impact of free energy contributions estimated to $\sim 1\text{-}3 \text{ kJ/mol}$ ^[25,26]

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

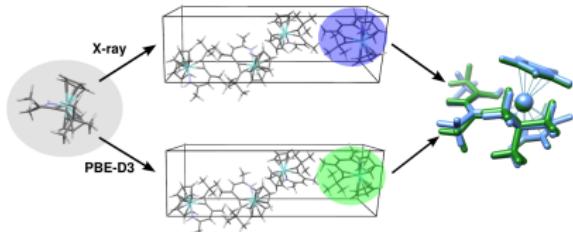
[26] JGB, S. Grimme *Acta Cryst. B*, **72**, 502 (2016)

Crystal packing dependent properties II

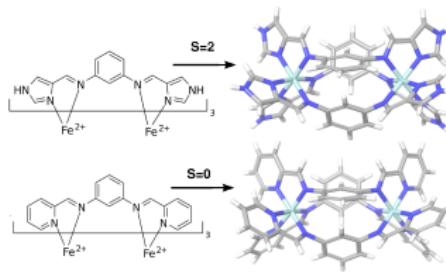


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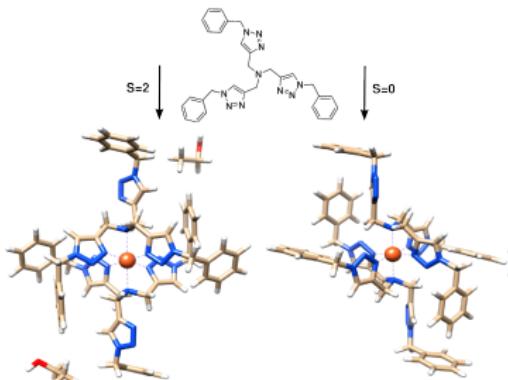
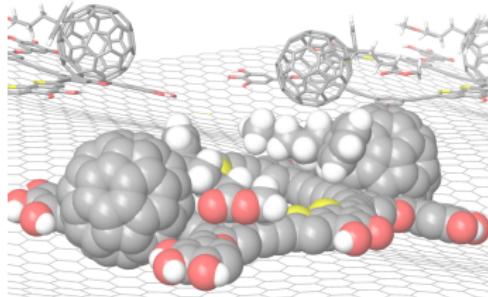
bond isomerization^[27]



spin crossover^[28]



co-adsorption on graphite



[27] JGB et al., *Organometallics*, **33**, 5358 (2014), [28] Schweinfurth et al., *Inorg. Chem.*, **53**, 8203 (2014)

Fast electronic structure for large systems

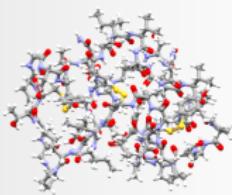


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gas phase protein

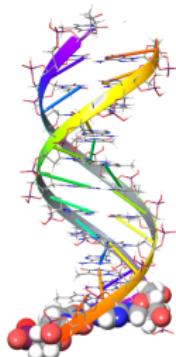
dim:
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wall time:
(HSE-3c on 16 cores)

0D
647 (647)
5h



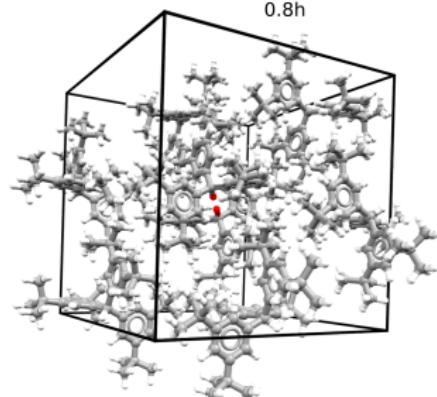
DNA helix

1D
726 (66)
0.5h



molecular crystal

3D
856 (37)
0.8h

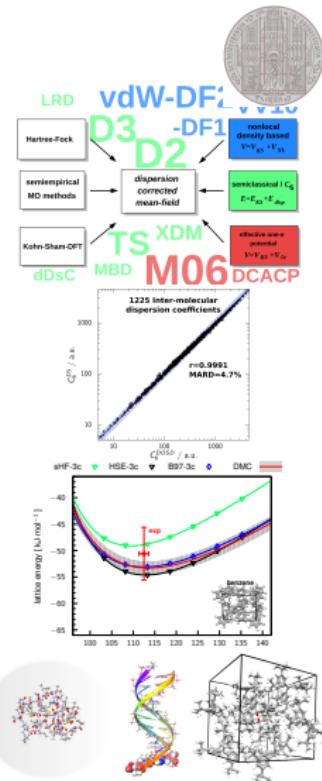


- fast computer code CRYSTAL17 with cost-efficient methods
- enabling routine electronic structure calculation of large systems

Summary

Take-home messages

- D3 London dispersion interaction arises in second order perturbation theory.
- C_6 based dispersion corrections are most efficient in DFT framework.
- DFT-D methods show excellent performance for organic crystals.
- D3, gCP, and composite methods implemented in CRYSTAL17



Key references



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

■ DFT development

R. Maurer, C. Freysold, A. Reilly, JGB, O. Hofmann, T. Björkman, S. Lebègue, A. Tkatchenko, *Annu. Rev. Mater. Res.* **49**, 1 (2019).

E. Caldeweyher, JGB, *J. Phys.: Condens. Matter* **30**, 213001 (2018).

L. Donà, JGB, M. Civalleri, *J. Chem. Phys.* **in press** (2018).

■ Crystal structure prediction:

L. Iuzzolino, P. McCabeb, S. L. Price, JGB, *Faraday Discuss.* **211**, 275 (2018).

■ website: gerit-brandenburg.de

twitter: [@JGBrandenburg](https://twitter.com/JGBrandenburg)