Density Functional Theory Including van der Waals Forces:

Semi-classical correction provides versatile electronic structure tool

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57TH SANIBEL SYMPOSIUM - ST. SIMONS ISLAND, GA, USA

London Centre for Nanotechnology
Department of Chemistry – University College London

Outline of talk

1. Introduction
2. Van der Waals inclusive density functional approximations
3. Beyond pure density functionals
4. Show-cases
5. Conclusions

Understanding phenomena in nature

How can a Gecko stick to a glass wall?

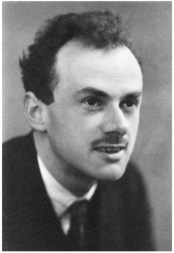
- cannot be explained by classical mechanics
- London dispersion (C_6)

Why does a tablet change its properties?

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

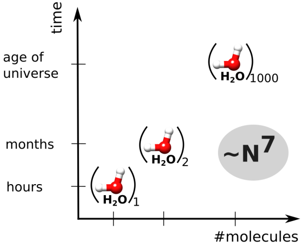
Exact simulation of extended systems computationally too demanding

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]



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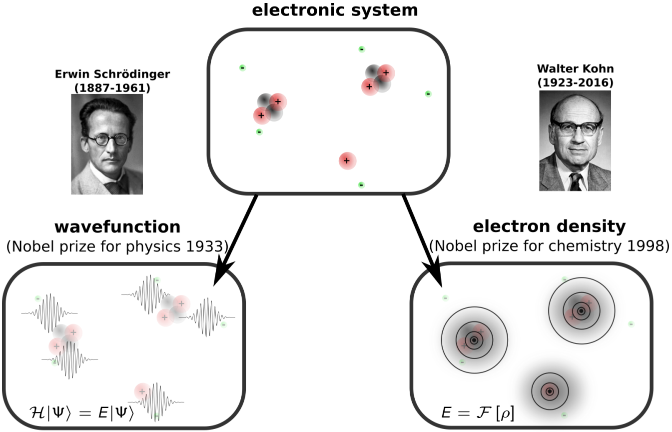
[1] P. A. M. Dirac, *Proc. Roy. Soc.Ser. A* **123**, 714 (1929)

Possible theoretical ansatz



electronic system

Erwin Schrödinger
(1887-1961)

Walter Kohn
(1923-2016)

wavefunction
(Nobel prize for physics 1933)

electron density
(Nobel prize for chemistry 1998)

$\mathcal{H}|\Psi\rangle = E|\Psi\rangle$

$E = \mathcal{F}[\rho]$

- exact in principle
- complicated to solve

- semi-local, easier to solve
- **no London dispersion**

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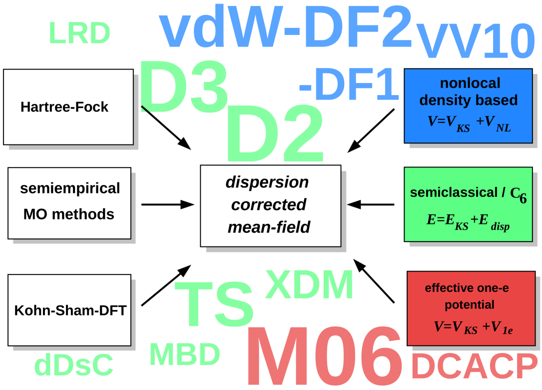
Many good dispersion corrections exist



LRD
vdW-DF2
VV10
D3
-DF1
D2
TS
XDM
M06
MBD
dDsC
DCACP

Hartree-Fock

semiempirical MO methods

Kohn-Sham-DFT

dispersion corrected mean-field

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

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

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

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

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[2] A. Stone *The Theory of Intermolecular Forces, 2nd ed.*; Oxford University Press, Oxford (2013)

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

Exact expression for correlation energy cannot be solved for many systems

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

- from adiabatic connection fluctuation dissipation theorem[4]
- Coulomb interaction scaled by λ
- dynamical charge density susceptibility

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

→ approximation needed

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[4] 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[5]

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

- C_8^{AB} and C_9^{AB} from recursion relations and averages[6]

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

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

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

Dynamic polarizability via linear response DFT

- use frequency domain formalism to get excitation frequencies[7]

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

- 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

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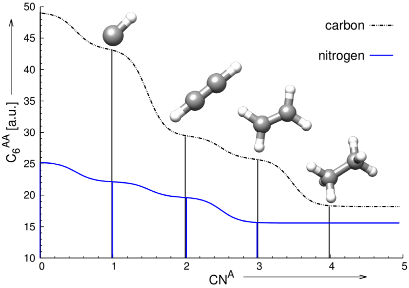
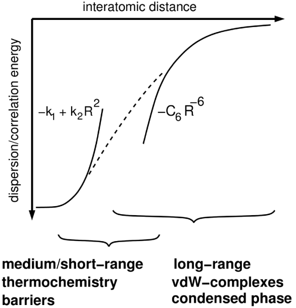
[7] M. E. Casida, *Recent Advances in Density Functional Methods*, D. P. Chong (World Scientific, Singapore), 155 (1995)

Geometric coordination number for interpolations of reference C_6





medium/short–range
thermochemistry
barriers

long–range
vdW–complexes
condensed phase

- 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[8]

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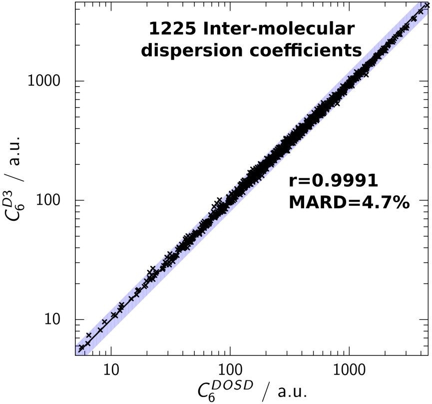
[8] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.*, **32**, 1456 (2011)

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 $< 5\%$ [9]
- deviations are close to intrinsic TD-DFT errors of $\alpha(i\omega)$

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

D3 in a nutshell: High accuracy at force field speed

Advantages of D3 model

- intermolecular C_6 coefficients are very accurate
- no electronic structure input needed
- computation is extremely fast D3(two-body) $\sim$ 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

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[*] See poster **Eike Caldeweyher**, Extension of the D3 dispersison coefficient model, 22st of Feb., 5:15 pm

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Lessons learned in the past years

- realistic structures are the key to many important physical and chemical properties

- Kohn-Sham density functional theory is method of choice for structures; wavefunction methods may take over for energies

- configurational sampling, entropy, and solvation issues are as important as good convergence in electronic energy

Multilevel methodologies: finding the right compromise

	task/property	**example method**
accurate QM	single-point energy	DLPNO-CCSD(T) DMC, FCIQMC
cheap QM	optimization	metaGGA (SCAN-D3[10]) HSE-3c[11,12]
very cheap QM	optimization/Hessians conformations	semi-empirical HF-3c[13,14], DFTB3-D3[15]
force field	dynamics conformational sampling	transferable or molecule specific (QM derived) FF

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

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

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

[13] R. Sure, S. Grimme, *J. Comput. Chem.*, **34**, 1672 (2013) [14] JGB, S. Grimme, *Top. Curr. Chem*, **345**, 1 (2014)

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

HSE-3c: Small basis DFT with semi-classical corrections

Requirements

- ∼10 × faster vs. standard DFA → small atomic orbital expansion
- reduce self-interaction error → use Fock exchange
- numerically robust → long-range screening of exchange

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

Technical details:[11]

- modified HSE[16] in small def2-mSVP[12] basis set
- D3 and gCP semi-classical corrections (7 global parameters)

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

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

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

DFTB3-D3: Dispersion corrected density functional tight-binding

Requirements

- $\sim 10^{3-4}$ × faster vs. standard DFA → neglect many-center integrals
- electronic eigenvalue problem → tight-binding Hamiltonian
- response to external field → self-consistent charges

$$E_{\text{tot}}^{\text{DFTB3-D3}} = E^{(\text{DFTB3})} + E_{\text{DISP}}^{(\text{D3})}$$

Technical details:[15]

- third order expansion in $\Delta\rho$, self-consistent charge redistribution[16]
- 3OB Slater-Koster parametrization with XH pair-damping[17]
- D3 semi-classical corrections, work on TS/MBD in progress

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

[16] B. Aradi, B. Hourahine, T. Frauenheim *J. Phys. Chem. A*, **111**, 5678-5684 (2007)

[17] M. Gaus, A. Goez, M. Elstner, *J. Chem. Theory Comput.* **9**, 338-354 (2013).

Atom-partitioned polarizability can be used for force field generation

Possible information from

- atom-in-molecule specific C_6 for dispersion interaction directly accessible in D3, for TS via geometric Hirshfeld construction[18]
- scaled atom radii for exchange repulsion
- atom-in-molecule static polarizability for induction interaction

Related work

- DMACRYS: distributed multipole based force field[19]
- QMDFF: quantum mechanically derived force field[20]
- CamCASP: atom-atom potentials from monomer and dimer properties[21]

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[18] T. Bereau,O. A. von Lilienfeld, *J. Chem. Phys.* **141**, 034101 (2014)

[19] S. L. Price, et al. *Phys. Chem. Chem. Phys.* **12**, 8478-8490 (2010)

[20] S. Grimme, *J. Chem. Theory Comput.* **10**, 4497-4514 (2014)

[21] A. J. Misquitta, A. J. Stone, *J. Chem. Theory Comput.* **12**, 4184-4208 (2016)

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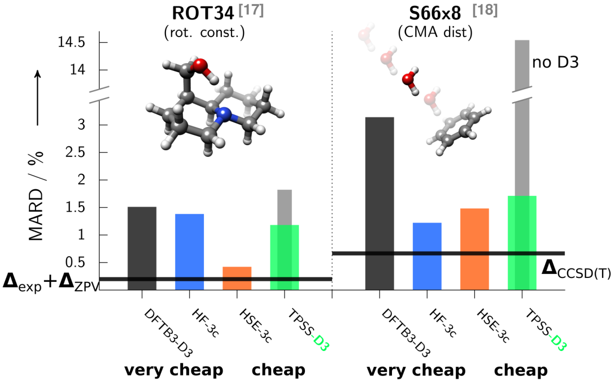
Systematically improvable bond length and molecular structures



- error estimates from measurement and theoretical back-correction
- significant effect of dispersion interaction

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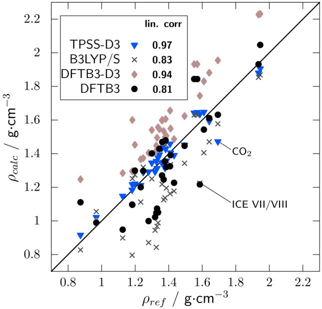
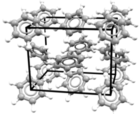
[17] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.*, **15**, 16031 (2013)

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

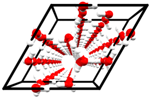
Good mass densities on diverse set of molecular crystals



X23 [19.20]



ICE10 [21]



- impact of zero-point and thermal contribution important
- outliers due to problematic induction effects

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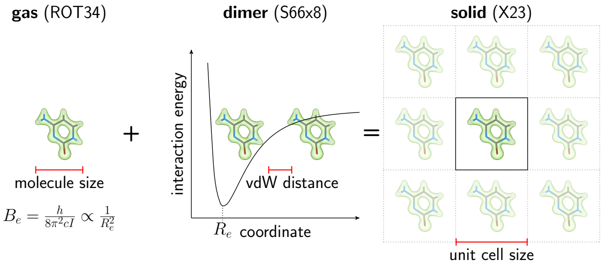
[19] E. Johnson, A. Otero-de-la-Roza, *J. Chem. Phys.* **137**, 054103 (2012)

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

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

Consistency for structures achieved



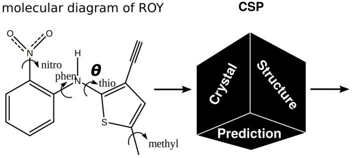
	ROT34 org. mol.	**S66x8** non-covalent	**X23** molecular crystal
TPSS/large basis	1.9	14.6	27.9
TPSS-D3/large basis	1.3	1.3	1.0
HF-3c (very cheap QM)	1.5	-1.2	-5.7
DFTB3-D3 (very cheap QM)	1.2	-2.9	-12.6
HSE-3c (cheap QM)	**0.2**	**1.3**	**0.7**

mean of relative deviation in %

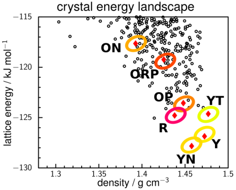
Sampling and energetic ranking for crystal structure prediction

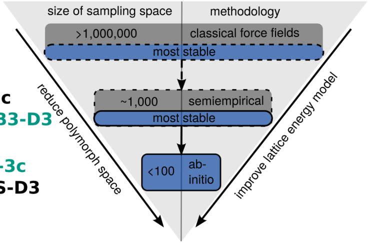
molecular diagram of ROY

CSP



crystal energy landscape





FF

HF-3c

DFTB3-D3

HSE-3c

TPSS-D3

size of sampling space | methodology

>1,000,000 | classical force fields

most stable

~1,000 | semiempirical

most stable

<100 | ab-initio

reduce polymorph space

improve lattice energy model

Properties
of ROY polymorphs

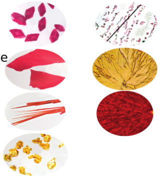
characterized **uncharacterized**

Red prism
P-1, θ=21.7°

Orange **R**ed **P**late
Pbca, θ=39.4°

Orange **N**eedle
$P2_1/c$, θ=52.6°

Yellow prism
$P2_1/n$, θ=104.7°



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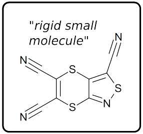
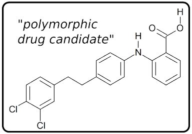
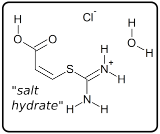
[22] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

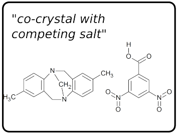
[23] M. Vasileiadis, A. V. Kazantsev, P. G. Karamertzanis, C. S. Adjiman, C. C. Pantelides, *Acta Cryst. B* **68**, 677 (2012)

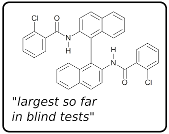
Promising results in the 6th blind test


"rigid small molecule"


"polymorphic drug candidate"


"salt hydrate"


"co-crystal with competing salt"


"largest so far in blind tests"

	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 ∼ 1-3 kJ/mol[24,25]

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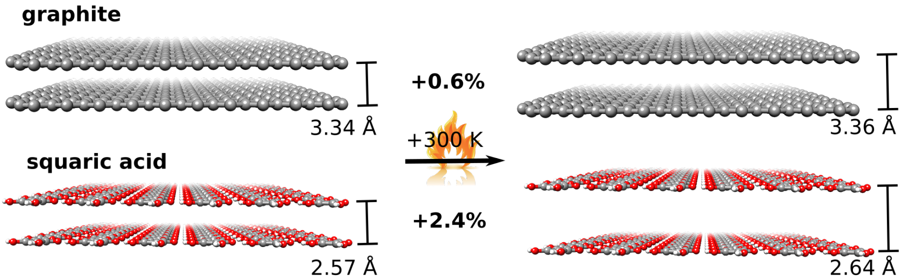
[24] A. Reilly, et al. *Acta Cryst. B*, **72**, 439 (2016)

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

Pronounced temperature effects on stacked 2D layers



- stacking distance of graphite 30% larger
- temperature effect of squaric acid 4 times larger

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[26] JGB, F. Fernandez-Alonso, A. Michaelides, S. L. Price, *in preparation.*

[27] G. Graziano, M. Gutmann, A. Michaelides, F. Fernandez-Alonso, *in preparation.*

Inelastic neutron scattering combined with HSE-3c phonon modes

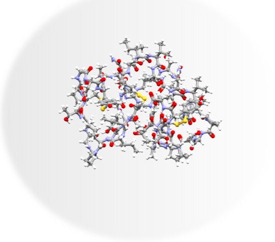
{non-published data}

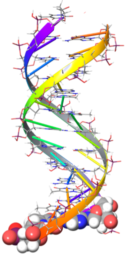
- pronounced out of plane bending of Hydrogens $\propto 1000\,\mathrm{cm}^{-1}$
- thermal expansion (QHA) in quantitative agreement with neutron scattering

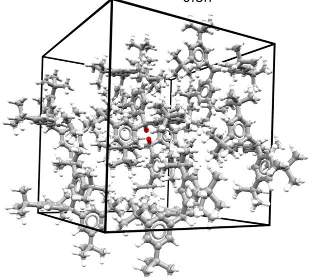
Fast electronic structure for large systems

	gas phase protein	**DNA helix**	**molecular crystal**
dim:	0D	1D	3D
#atoms/unit:	647 (647)	726 (66)	856 (37)
wall time:	5h	0.5h	0.8h

(**HSE-3c** on 16 cores)







- fast computer code CRYSTAL17[26] with cost-efficient methods[11]
- enabling routine electronic structure calculation of large systems

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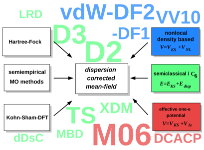
[26] R. Dovesi, et al., *Int. J. Quantum Chem.*, **114**, 1287-1317 (2014)

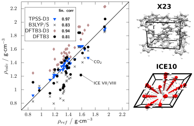
[11] JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.*, **18**, 15519 (2016)

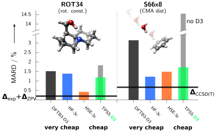
Summary


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

Conclusions

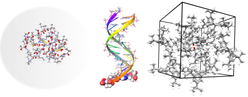
- D3 dispersion correction can be combined with various methods
- cheap QM methods (HSE-3c, DFTB3-D3) useful for fast electronic structures
- promising results of crystal energy rankings in CSP blind test





Outlook and possible improvements

- exploring the merit of DFT-D methods in context of CSP further
- benchmark energies for organic solids
- analysis of phonon spectra, free energies



Acknowledgements

Collaborators

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