Organic crystal modeling:
A hierarchy of quantum chemical methods

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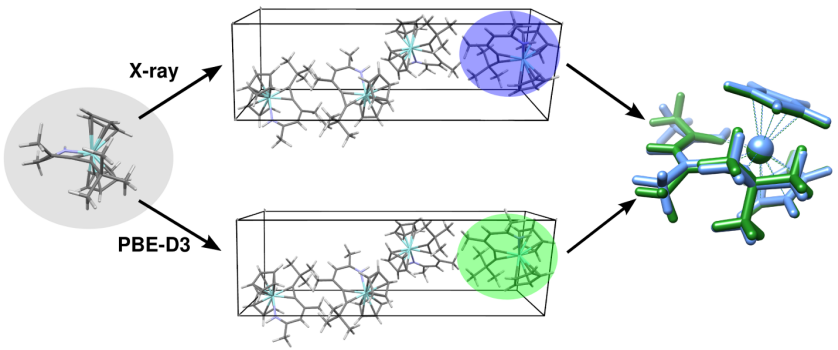
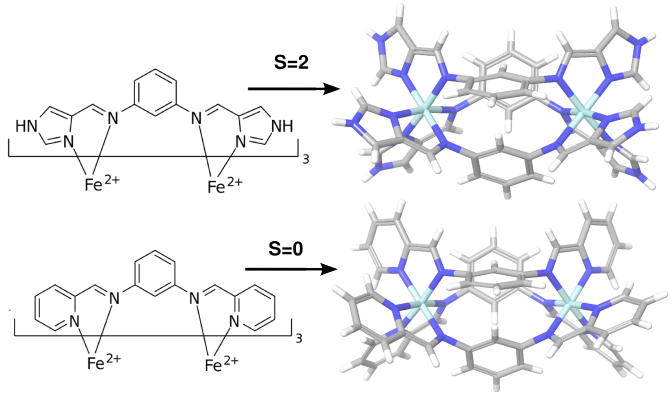
Crystal packing dependent properties

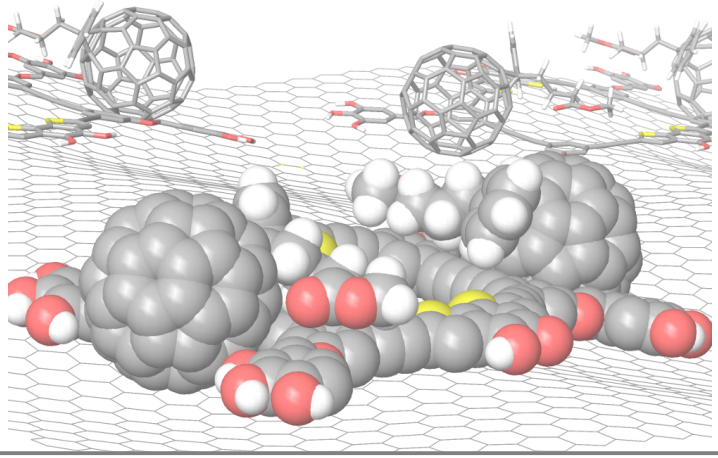
bond isomerization[1]

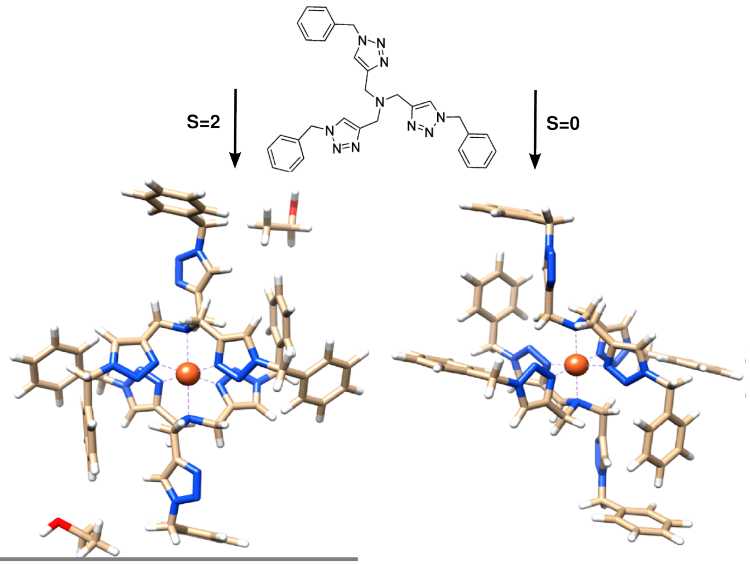


spin crossover[2]



co-adsorption on graphite

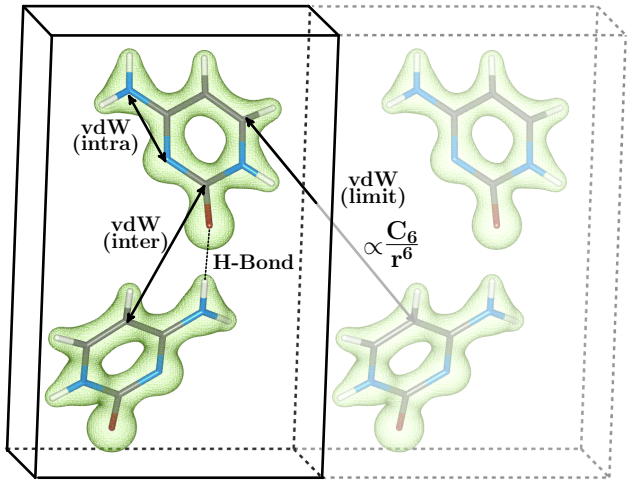




[1] JGB et al., *Organometallics*, **33**, 5358 (2014), [2] Schweinfurth et al., *Inorg. Chem.*, **53**, 8203 (2014)

Intermolecular interactions

- Pauli exchange repulsion
- electrostatic
- induction
- London dispersion



- compromise between accuracy and computational efficiency[3,4,5]

[3] J. Yang, W. Hu, D. Usvyat, D. Matthews, M. Schütz, G. Chan, *Science*, **345**, 640 (2014)

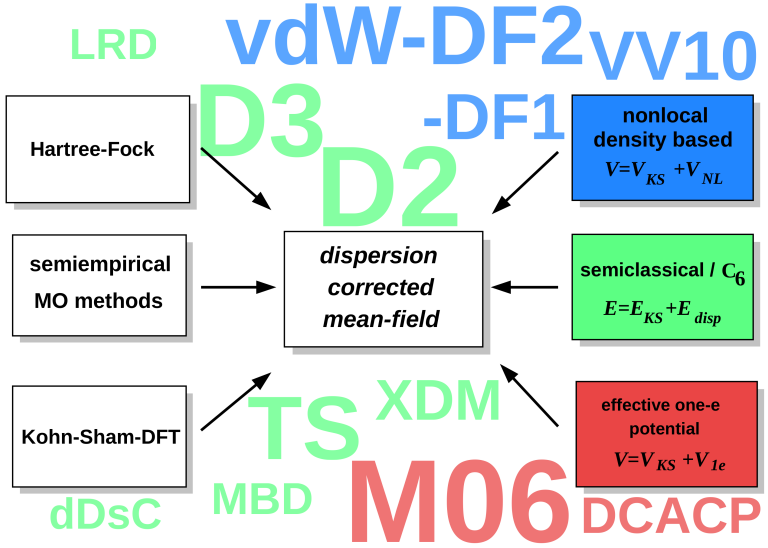
[4] JGB, S. Grimme, *Top Curr Chem*, **345**, 1 (2014)

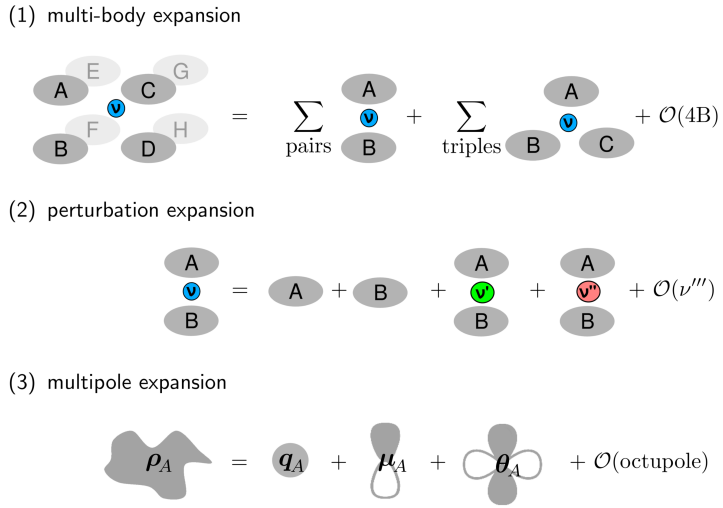
[5] JGB, M. Hochheim, T. Bredow, S. Grimme, *J. Phys. Chem. Lett.* **5**, 4275 (2014)

Intermolecular interactions

Formally exact expression vs. pratical approaches[6]

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





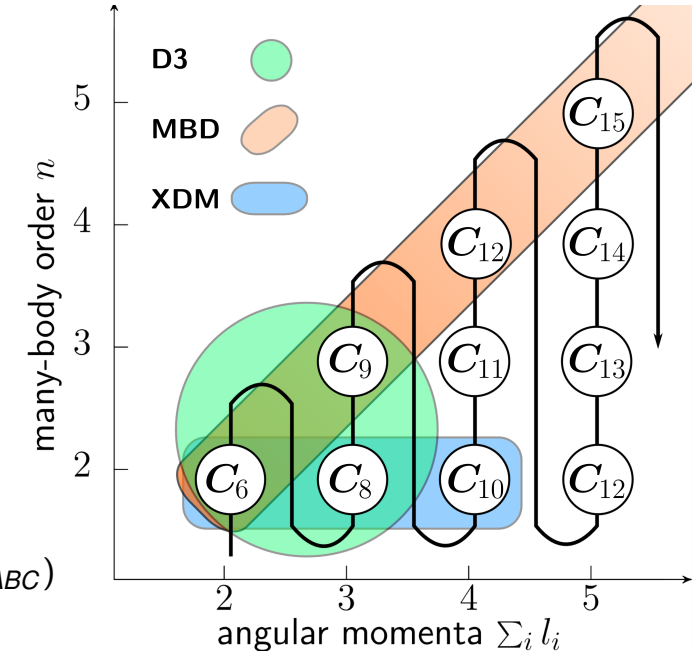
[6] S. Grimme, A. Hansen, JGB, C. Bannwarth, *Chem. Rev.*, DOI: 10.1021/acs.chemrev.5b00533 (2016)

London DISP and BSSE

D3: dispersion correction[7]

- third order in many-body expansion
- quadrupole terms in multipole expansion

$$E_{\mathrm{disp}}^{(\mathrm{D3})} = -\frac{1}{2}\sum_{n=6,8}\sum_{A,B}^{\mathrm{pairs}}\frac{C_n^{AB}}{r_{AB}^n}\cdot f_n^d(r_{AB}) - \frac{1}{6}\sum_{A,B,C}^{\mathrm{triples}}\frac{C_9^{ABC}\,(1+3\cos\theta_A\cos\theta_B\cos\theta_C)}{r_{ABC}^9}\cdot f_9^d(r_{ABC})$$



gCP: geometric counterpoise correction[8,9]

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

[8] H. Kruse, S. Grimme, *J. Chem. Phys.*, **136**, 154101 (2012)

[9] JGB, M. Alessio, B. Civalleri, M. Peintinger, T. Bredow, S. Grimme, *JPC A*, **117**, 9282 (2013)

Multilevel methodologies

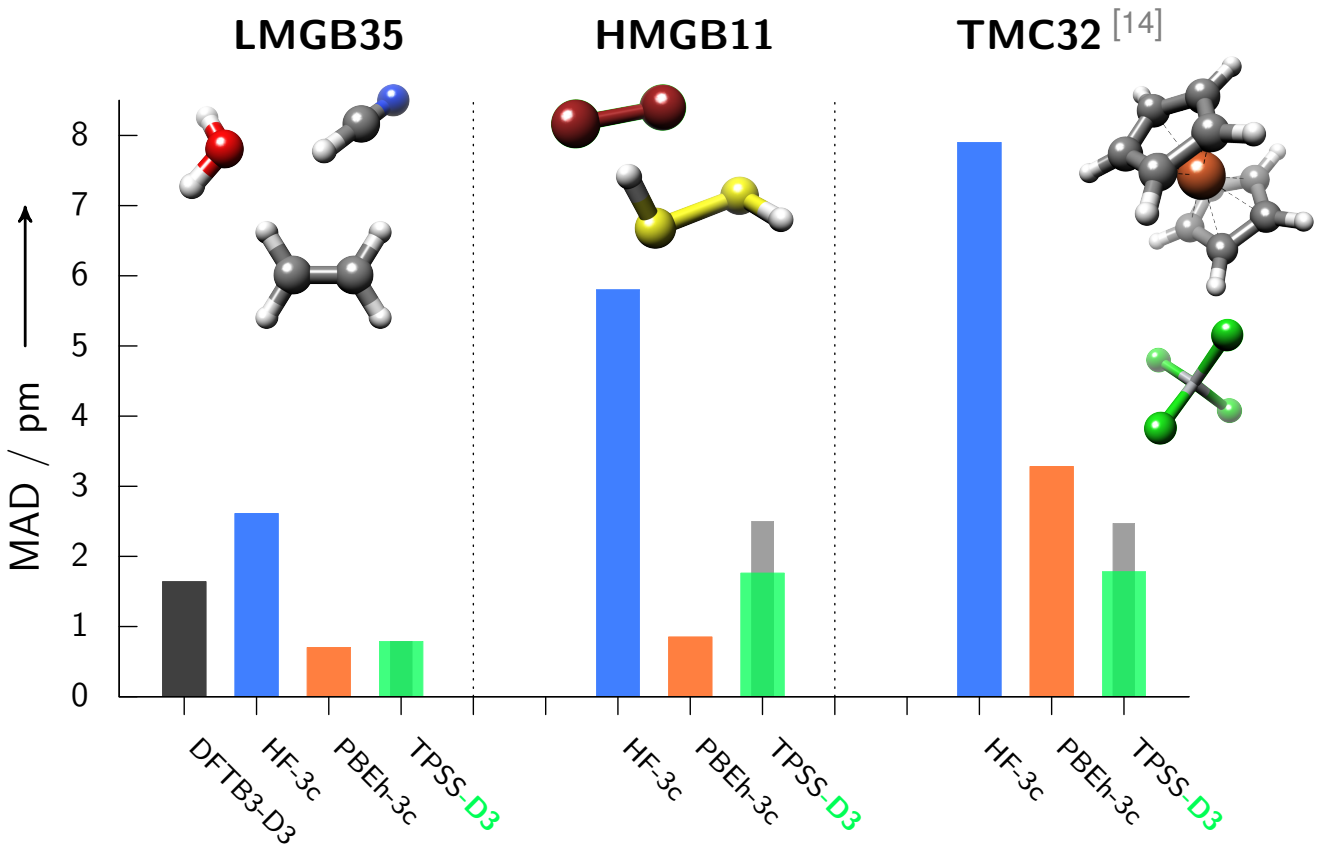
	basis set	DISP	BSSE	additional
TPSS-D3	'CBS'	D3^{atm}	–	–
⇓ $\times 10^1$ speed-up				
PBEh-3c[10] & **HSE-3c**[11]	DZ	D3^{atm}	gCP	mod. E_{XC}
⇓ $\times 10^1$				
HF-3c[12]	minimal	D3^{atm}	gCP	SRB
⇓ $\times 10^2$				
DFTB3-D3[13]	minimal	D3^{atm}	–	HX-damping, SK splines

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

[11] JGB, E. Caldeweyher, S. Grimme, *PCCP*, (submitted) [12] R. Sure, S. Grimme, *J. Comput. Chem.*, **34**, 1672 (2013)

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

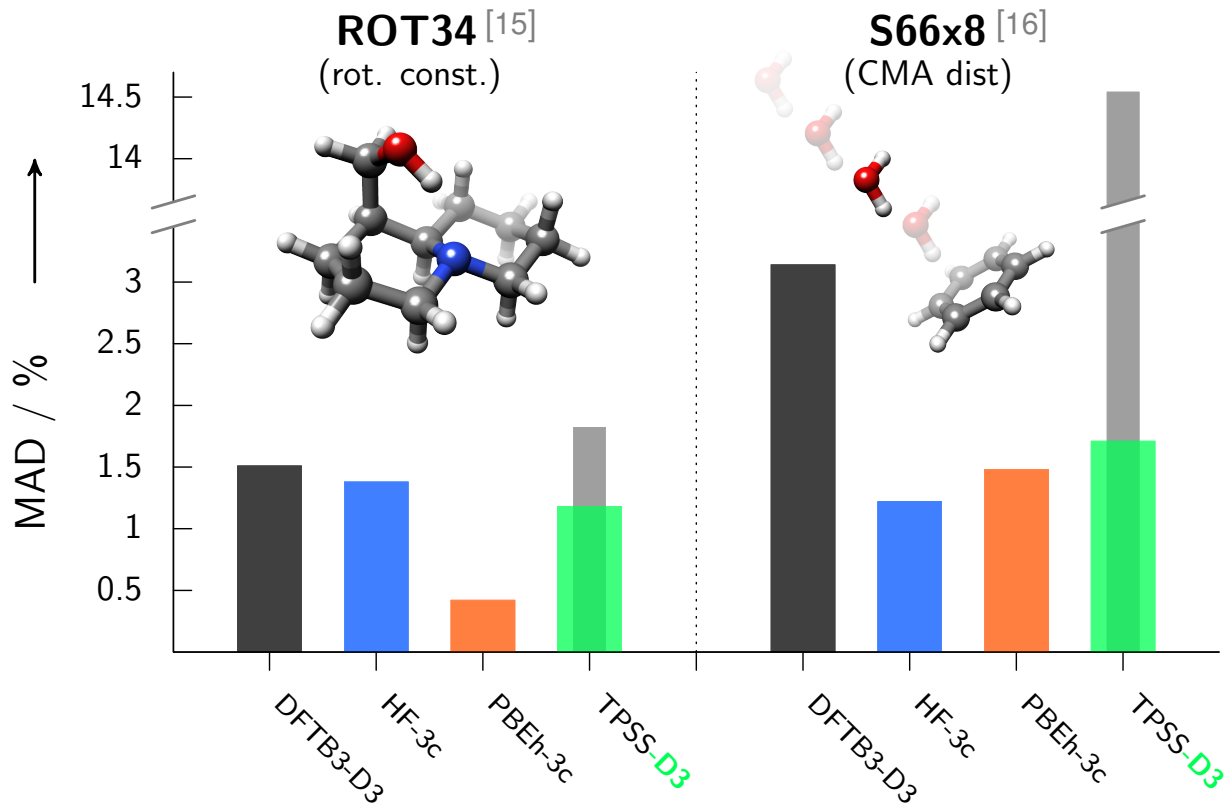
Covalent bond lengths



- Fock exchange problematic for 3d complexes

[14] M. Bühl, H. Kabrede, *J. Chem. Theory Comput.*, **2**, 1282 (2006)

Noncovalent bonds length



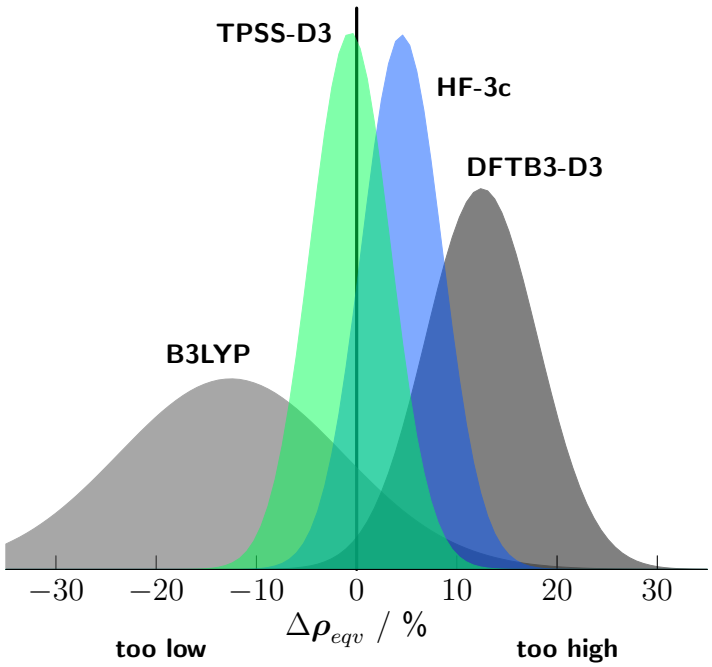
- significant effect of dispersion interaction

[15] S. Grimme, M. Steinmetz, *Phys. Chem. Chem. Phys.*, **15**, 16031 (2013)
[16] J. Rezáč, K. Riley, P. Hobza, *J. Chem. Theory Comput.*, **8**, 2427 (2011)

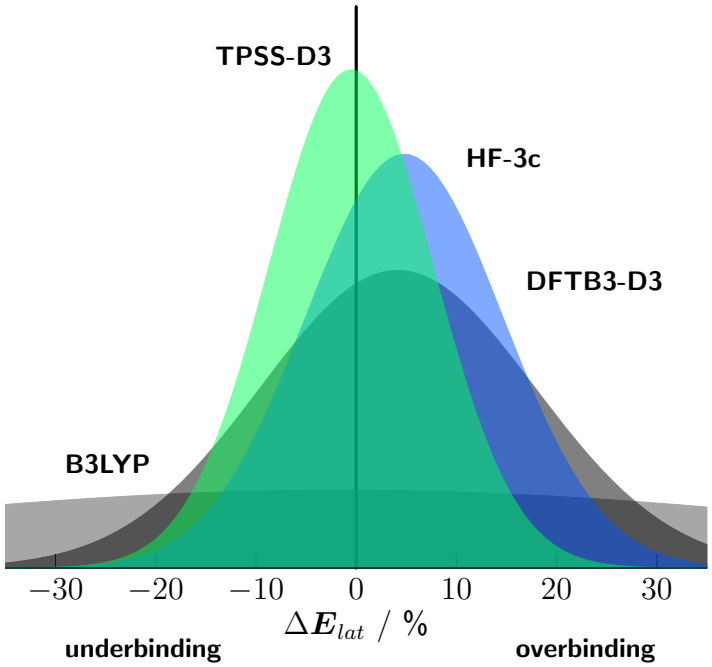
NCI: molecular crystals

X23[17,18] and **ICE10**[19] solid state benchmark sets

geometries



energies

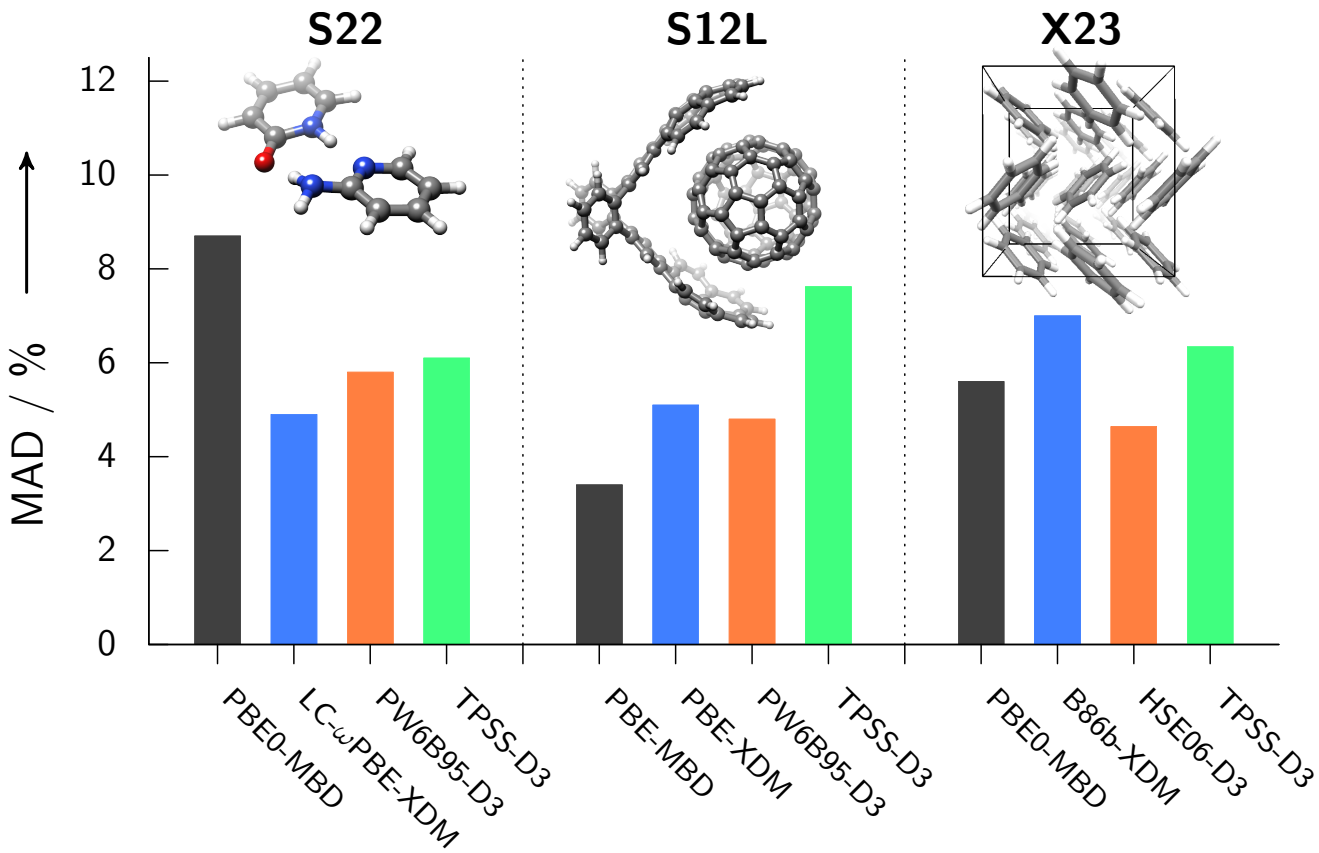


[17] E. Johnson, A. Otero-de-la-Roza, *J. Chem. Phys.* **137**, 054103 (2012)

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

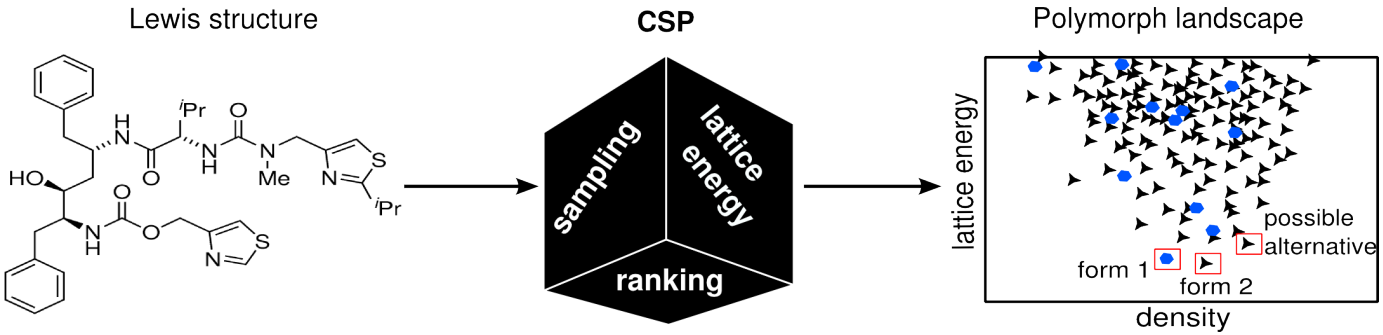
[19] JGB, T. Maas, S. Grimme, *J. Chem. Phys.* **142**, 124104 (2015)

Performance of dispersion models



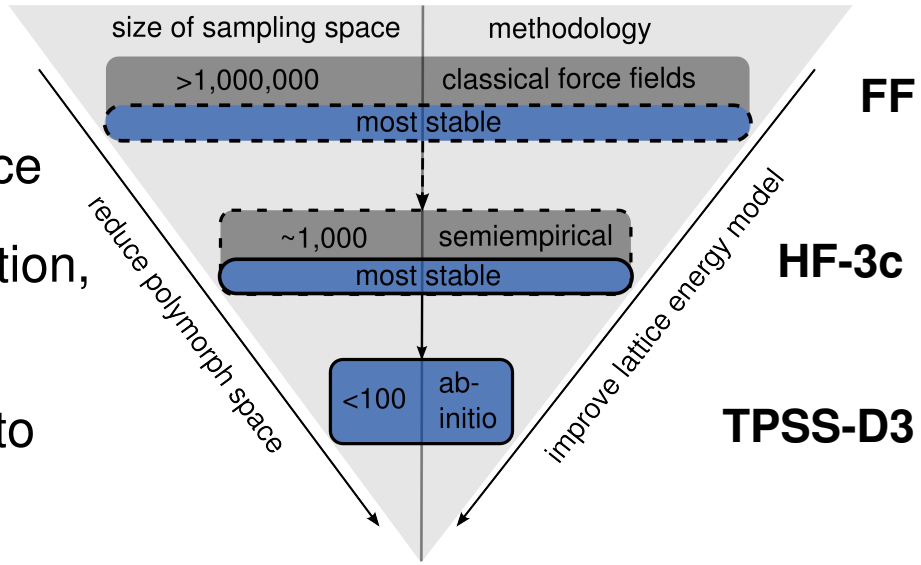
- error in S12L and X23 reference about 3-5%
- different dispersion corrected DFAs yield high quality results

Crystal structure prediction challenge



Layers of complexity:

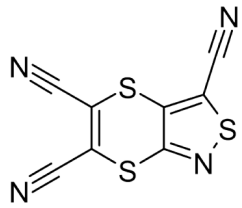
- molecular conformational space
- space groups (varying orientation, conformation, etc.)
- polymorph ranking according to free energy[20,21]



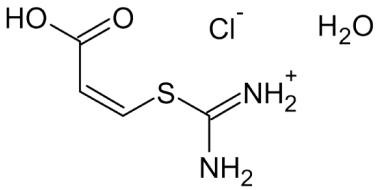
[20] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

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

Blind test results



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



exp. polymorph: **Rank 1**
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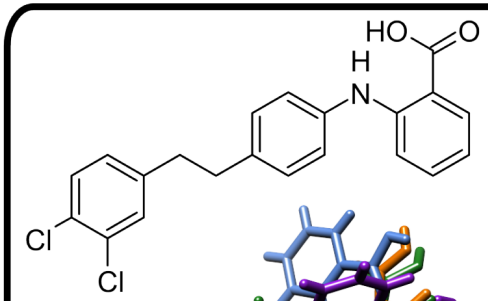
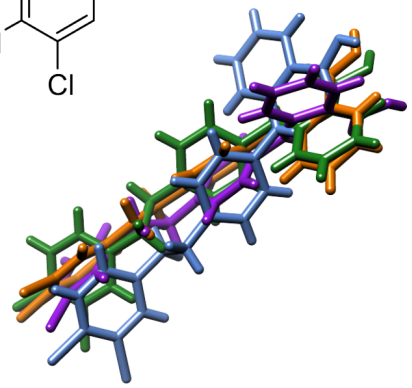
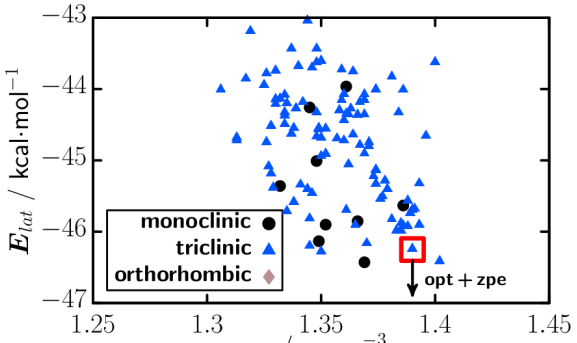
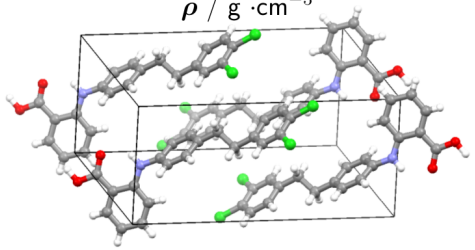
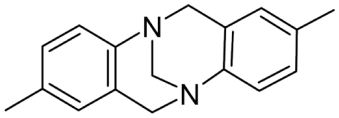


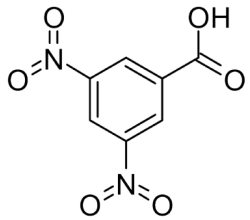




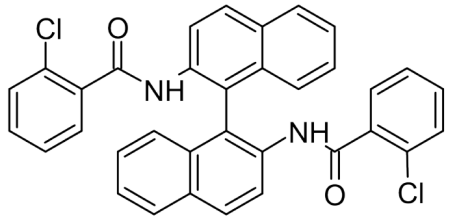


exp. polymorph: **Ranks 1-10**
found in sampling: ✓ / ✗





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



exp. polymorph: **Rank 1** found: ✗

[22] A. Reilly, et al. *Acta Cryst. B*, submitted

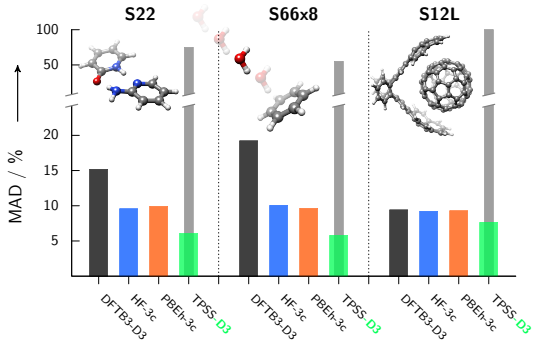
Summary

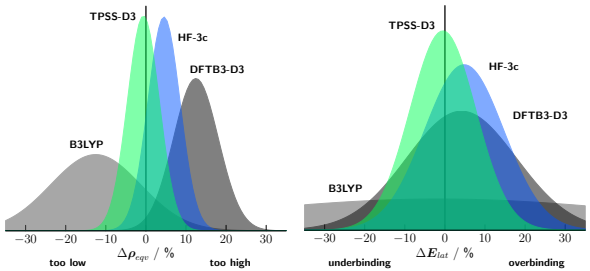
Conclusions

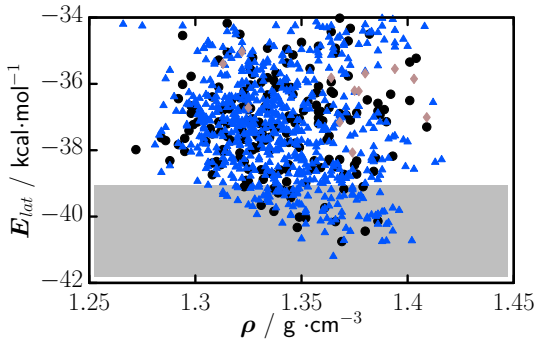
- hierarchy of electronic structure methods
- simplified methods could bridge the gap between FF and DFT
- HF-3c and TPSS-D3 for crystal structure prediction

Outlook and possible improvements

- apply higher levels for final ranking
- improve FF$\longrightarrow$HF-3c transition







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Collaborators

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AvH goals

- connecting academic excellence worldwide
- knowledge transfer and cooperation at the highest level
- strengthening cutting-edge research through internationalization

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postdoctoral researchers

PhD completed less than 4 years ago

- Research fellowship: 6-24 month with German host

junior group leaders

PhD completed less than 6 years ago

- Sofia Kowalewskaja award: own research group in Germany

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experienced researcher

PhD completed less than 12 (18) years ago

- Research fellowship: 6-18 month with German host
- Friedrich Wilhelm Bessel Award: research stay in Germany

international cutting-edge researcher

- Humboldt research award and Alexander von Humboldt Professorship

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