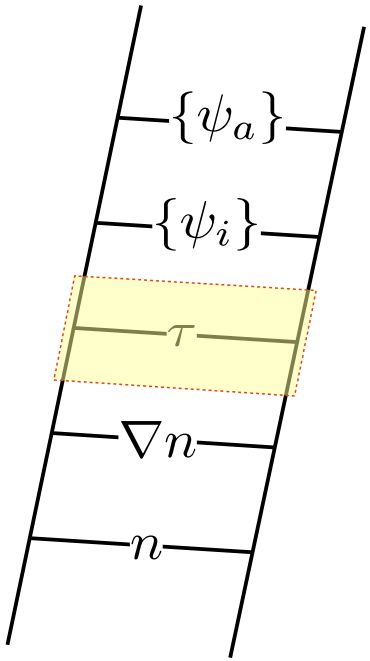
Meta-GGAs in ONETEP

(Briefly)

ONETEP Masterclass 2017, Aug/Sep 2017



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Linear-scaling density functional theory

- Orthogonalize KS orbitals extending over entire system
- Cubically scaling computational cost

$$\mathcal{O}(N^3)$$

Conventional Kohn-Sham DFT

$$\mathrm{E}_{\mathrm{KS}}[n] = T_{\mathrm{s}}[n] + E_{\mathrm{ext}}[n] + E_{\mathrm{Hartree}}[n] + E_{\mathrm{xc}}[n]$$

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Linear-scaling density matrix DFT

$$\rho(\mathbf{r},\mathbf{r}') = \sum_i^N f_i\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')$$

$$\rho(\mathbf{r},\mathbf{r}) = n(\mathbf{r})$$

$$T_{\mathrm{s}}[n] = \int \mathrm{d}\mathbf{r}\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2\rho(\mathbf{r},\mathbf{r}')\right]_{\mathbf{r}=\mathbf{r}'}$$

$$\mathcal{O}(N)$$

- The density matrix is "nearsighted"
- For insulators:*

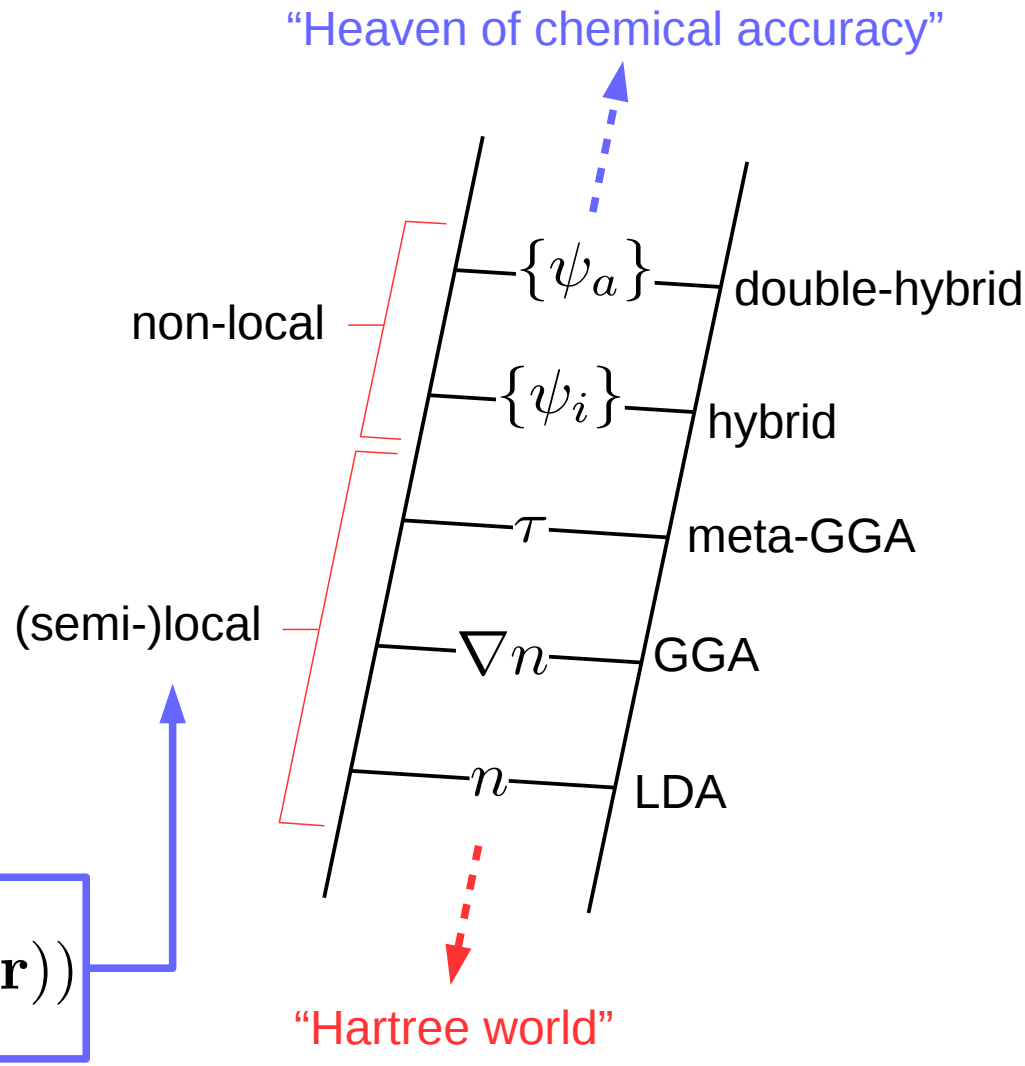
$$\rho(\mathbf{r},\mathbf{r}') \sim \mathrm{e}^{-\gamma|\mathbf{r}-\mathbf{r}'|}$$

- Exploit this to obtain linear scaling computational cost

*see e.g. S. Ismail-Beigi and T.A. Arias, Phys. Rev. Lett. **82**, 2127 (1999)

Approximate exchange-correlation functionals

- No practical exact form is known
  - Approximations are required
- Ideally, these should be
  - Accurate
  - Computationally efficient
- “Jacob's ladder” of approximations
  - Hierarchical series
  - New ingredients on each “rung”
  - Higher rungs are more flexible
- Which is the best tool for the job?

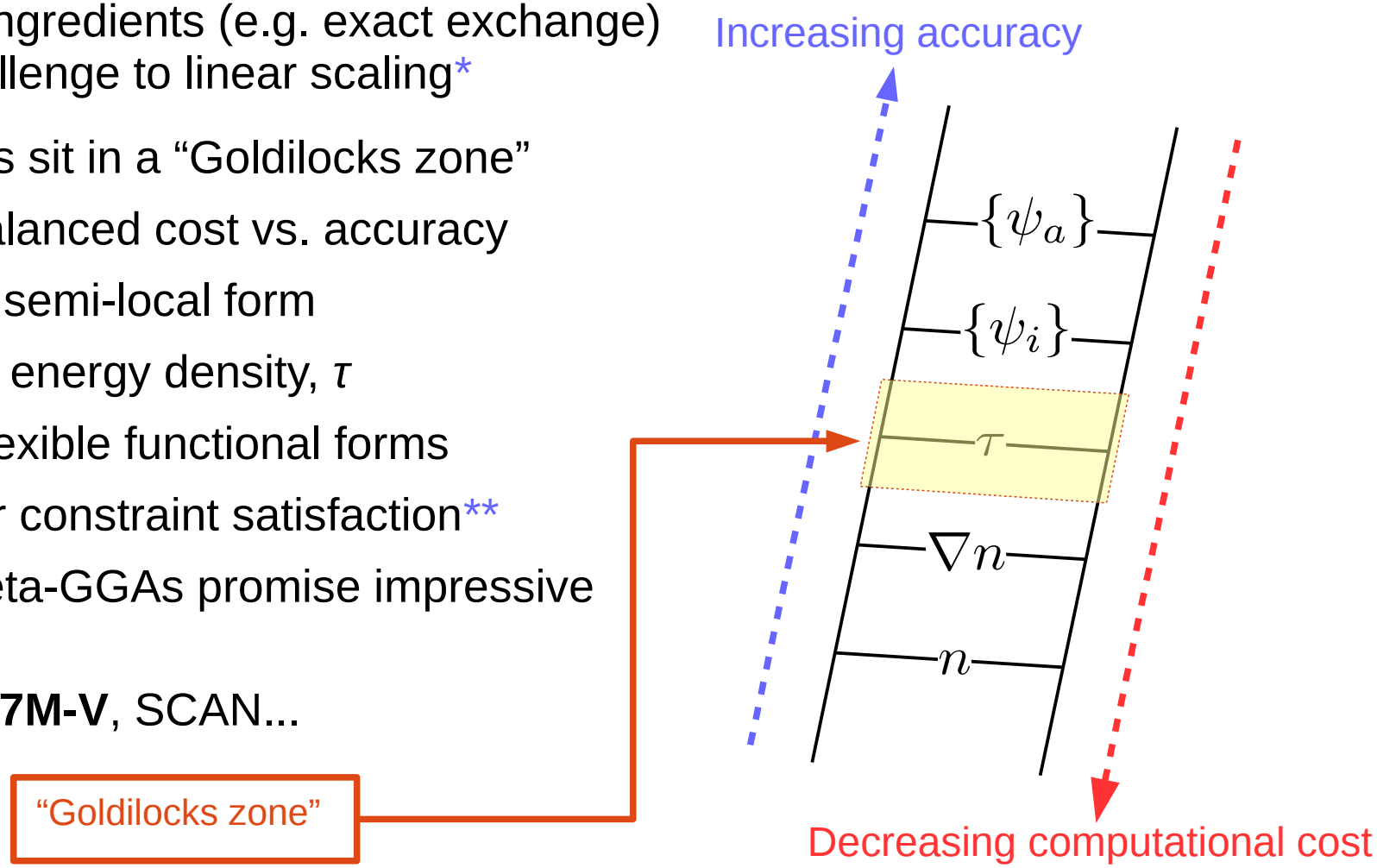


$$E_{\mathrm{xc}}[n] = \int \mathrm{d}\mathbf{r}\, \epsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r}))$$

J.P. Perdew and K. Schmidt, AIP Conf. Proc. **577**, 1 (2001)

Motivation: The meta-GGA “Goldilocks zone”

- Non-local ingredients (e.g. exact exchange) pose a challenge to linear scaling*
- Meta-GGAs sit in a “Goldilocks zone”
  - Well-balanced cost vs. accuracy
  - Simple semi-local form
- Add kinetic energy density, τ
  - More flexible functional forms
  - Greater constraint satisfaction**
- Modern meta-GGAs promise impressive accuracy
  - e.g. **B97M-V**, SCAN...



* Linear scaling exact exchange has been achieved in ONETEP but with a relatively large prefactor:
J. Dziedzic, Q. Hill, and C.-K. Skylaris,
J. Chem. Phys. **139**, 214103 (2013)

** For more on constraint satisfaction:
J.P. Perdew, A. Ruzsinszky, J. Tao,
V.N. Staroverov, G.E. Scuseria, and G.I. Csonka,
J. Chem. Phys. **123**, 62201 (2005)

Self-consistent meta-GGA evaluation

$$V_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}}{\delta n(\mathbf{r})} = \frac{\delta}{\delta n(\mathbf{r})} \int \mathrm{d}\mathbf{r}\, \epsilon_{\rm xc}(n, \nabla n, \tau[n]) \dashrightarrow \frac{\delta \tau[n]}{\delta n(\mathbf{r})} = ?$$

Functional **D**erivatives (of τ-dependent functionals) with respect to the **O**rbitals*

Use the functional derivative chain rule to obtain

$$\frac{\delta E_{\rm xc}^{\rm mGGA}}{\delta \psi_i(\mathbf{r})} = \int \mathrm{d}\mathbf{r}' \frac{\delta E_{\rm xc}^{\rm mGGA}}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta \psi_i(\mathbf{r})}$$

The functional derivative

$$\frac{\delta n(\mathbf{r}')}{\delta \psi_i(\mathbf{r})} = 2\psi_i(\mathbf{r})\delta(\mathbf{r}' - \mathbf{r})$$

allows us to derive the following relationship

$$\frac{1}{2}\frac{\delta E_{\rm xc}^{\rm mGGA}}{\delta \psi_i(\mathbf{r})} = \frac{\delta E_{\rm xc}^{\rm mGGA}}{\delta n(\mathbf{r})}\psi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2$$

$$\tau(\mathbf{r}) = \frac{1}{2}\sum_{i}^{N_{\rm occ}} |\nabla\psi_i(\mathbf{r})|^2$$

Advantages of the approach

- Theoretical simplicity
- Computational simplicity
- Wide use in other code

* AKA “NNH” approach after the creators:
R. Neumann, R.H. Nobes, and N.C. Handy,
Mol. Phys. **87**, 1 (1996)

For a detailed account, see:
F. Zahariev, S.S. Leang, and M.S. Gordon,
J. Chem. Phys. **138**, 244108 (2013)

Functionals

PKZB

- An early meta-GGA (1999)
  - 1 empirical parameter
  - Evolved into TPSS (2003)
- Simple to implement
  - Based on PBE, but with τ
- Widely available
  - Stable implementations to compare and test against
- Inconsistent accuracy
  - Superseded by modern meta-GGAs

J.P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999)

B97M-V

- Modern meta-GGA (2015)
  - Combinatorially designed form
  - Empirically fitted to very large data set
- Incorporates non-local VV10 functional
  - Available in ONETEP
- Excellent accuracy
  - Comparable to popular hybrid functionals
  - Broadly applicable
- Code provided by N. Mardirossian

N. Mardirossian and M. Head-Gordon, J. Chem. Phys. **142**, 074111 (2015)

Aside: How good is B97M-V?

Thermochemical data

	RMSD	Hybrid
M06-2X	3.21	✓
ωB97X-V	3.60	✓
ωB97X-D	3.61	✓
B97M-V	3.93	
B97-D2	3.97	✓
M11	3.97	✓
M06	4.18	✓
B3LYP-D3	4.66	✓
M06-L	5.63	
TPSS-D3	6.45	
VV10	9.81	
PBE-D3	10.10	
Zero	3836.93	

aQZ basis set

2460 data points

Performs well against hybrid functionals!

NLC is not sufficient for good performance in either set

Non-covalent data

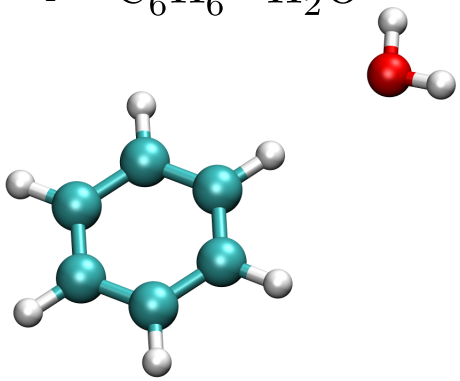
	RMSD	Hybrid
B97M-V	0.22	
ωB97X-V	0.32	✓
M06-L	0.42	
B97-D2	0.48	✓
ωB97X-D	0.54	✓
M11	0.55	✓
M06	0.57	✓
M06-2X	0.77	✓
B3LYP-D3	0.77	✓
TPSS-D3	0.85	
PBE-D3	1.23	
VV10	1.36	
Zero	14.95	

aTZ basis set

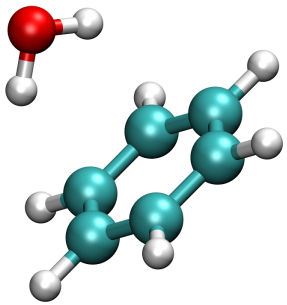
RMSDs in kcal/mol for thermochemical and non-covalent datasets (combined training and test data).
Based on Table V of N. Mardirossian and M. Head-Gordon, J. Chem. Phys. **142**, 074111 (2015).

Results: Binding energies

I $C_6H_6\cdots H_2O$

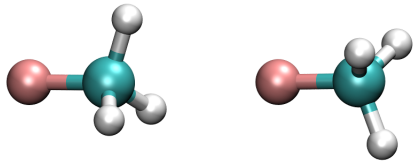


II $C_6H_6\cdots H_2O$

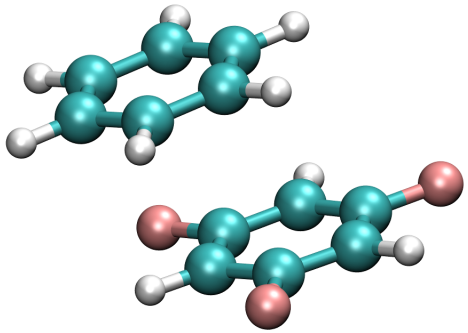


PBE	Q-Chem def2-QZVPPD	ONETEP 900 eV / 8 bohr	ONETEP 1200 eV / 12 bohr
I	-0.922	-0.920	-0.925
II	-1.790	-1.706	-1.775
III	-0.925	-0.963	-0.957
IV	0.650	0.856	0.794
RMSD		0.113	0.074
PKZB	**Q-Chem**	**ONETEP**	**ONETEP**
I	0.026	-0.011	-0.034
II	-0.572	-0.716	-0.790
III	-0.528	-0.607	-0.619
IV	1.221	1.014	0.956
RMSD		0.133	0.180
B97M-rV*	**Q-Chem**	**ONETEP**	**ONETEP**
I	-1.214	-1.246	-1.249
II	-3.283	-3.249	-3.329
III	-1.435	-1.496	-1.497
IV	-4.508	-4.358	-4.443
RMSD		0.084	0.053

III $CH_3F\cdots CH_3F$



IV $C_6H_3F_3\cdots C_6H_6$

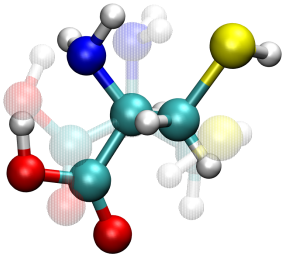


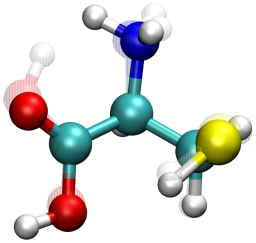
Binding energies in kcal/mol. RMSDs relative to Q-Chem

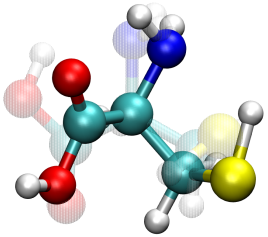
***"rV" refers to revised VV10: R. Sabatini, T. Gorni, and S. de Gironcoli, Phys. Rev. B **87**, 041108 (2013).
I, **II** structures (HW30): K.L. Copeland and G.S. Tschumper, J. Chem. Theory Comput. **8**, 1646 (2012).
III, **IV** structures (X40): J. Řezáč, K.E. Riley, and P. Hobza, J. Chem. Theory Comput. 8, 4285 (2012).

Results: Conformational energies

Cysteine

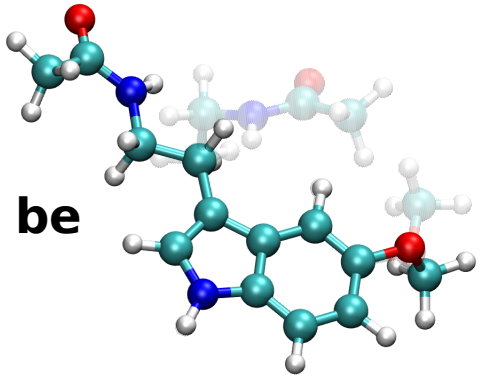
II 

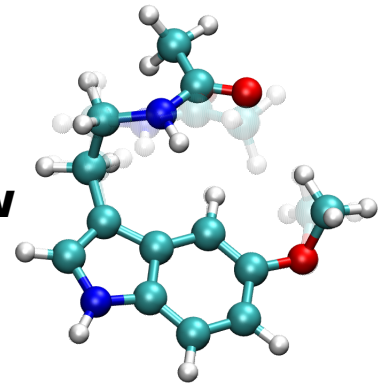
III 

IV 

PBE	Q-Chem def2-QZVPPD	ONETEP 900 eV / 8 bohr	ONETEP 1200 eV / 12 bohr
II	0.894	0.910	1.013
III	3.033	3.261	3.292
IV	3.161	3.385	3.339
be	4.487	4.489	4.521
dw	6.319	6.125	6.469
RMSD		0.167	0.165
PKZB	**Q-Chem**	**ONETEP**	**ONETEP**
II	0.744	0.745	0.867
III	1.194	1.565	1.573
IV	2.102	2.484	2.212
be	4.853	5.316	4.972
dw	5.939	6.163	6.358
RMSD		0.331	0.268
B97M-rV	**Q-Chem**	**ONETEP**	**ONETEP**
II	1.481	1.528	1.699
III	1.313	1.427	1.664
IV	1.481	1.683	1.863
be	5.582	5.193	5.909
dw	9.424	9.011	9.731
RMSD		0.275	0.322

Melatonin

be 

dw 

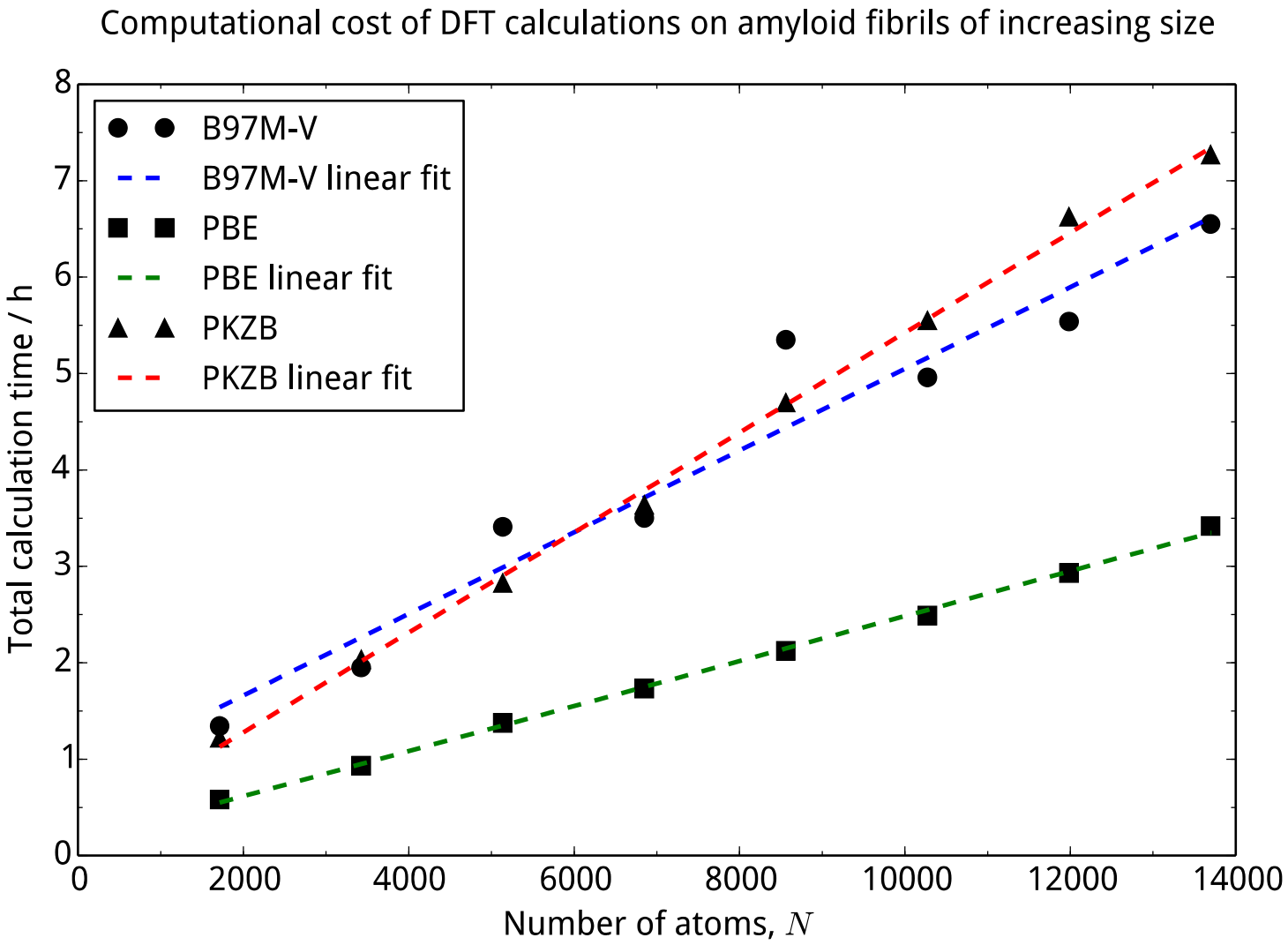
- Conformational energies in kcal/mol.
- RMSDs relative to Q-Chem.

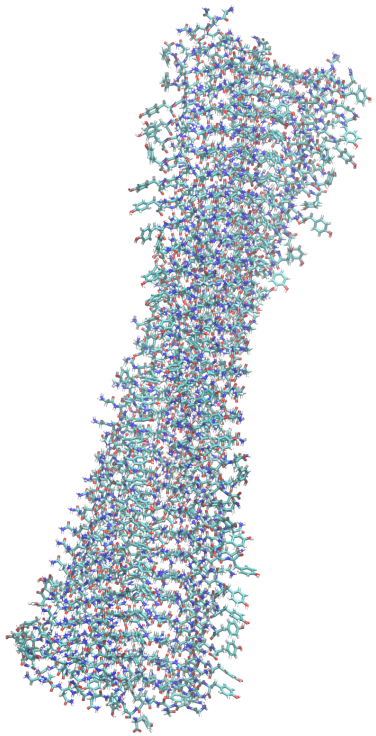
Relative to lowest energy conformers:

- Cysteine **I**
- Melatonin **aa**

Cysteine structures: L. Goerigk and S. Grimme, J. Chem. Theory Comput. **7**, 291 (2011)
Melatonin structures: U.R. Fogueri, S. Kozuch, A. Karton & J.M.L. Martin, J. Phys. Chem. A **117**, 2269 (2013)

Results: Computational efficiency





13696 atom structure

- Iridis 4 supercomputer
- 128 MPI processes
- 4 OpenMP threads

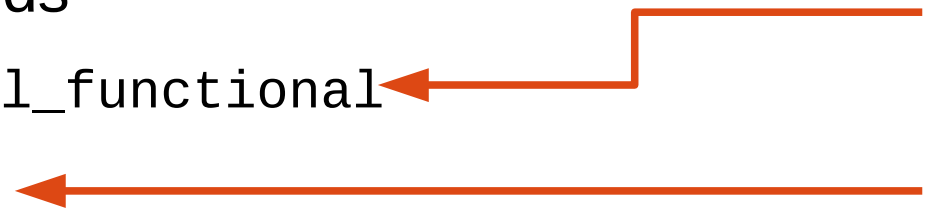
Structure provided by authors of J.T. Berryman, S.E. Radford, and S.A. Harris, Biophys. J. **97**, 1 (2009)

Conclusions

- Self-consistent meta-GGA functional evaluation in ONETEP
  - Theoretical and computational framework implemented and tested
  - Further functional forms can easily be added
  - Meta-GGAs can be applied to very large systems
- Numerical agreement with other implementations
  - Comparable agreement to well-tested GGA functionals
- Linear-scaling computational cost
  - Self-consistent evaluation of meta-GGA functionals
  - Demonstrated for systems with 1000s of atoms

Practical considerations

- Meta-GGA functionality is still under development
  - Only PKZB and B97M-V implemented
  - Not compatible with some other parts of ONETEP (e.g. PAW)
- To use a meta-GGA, use
  - `xc_functional: PKZB`
  - `xc_functional: B97M-V`
- Other keywords
  - `xc_initial_functional`
  - `xc_mintau`
- Input examples can be found in test directory (56 and 57)



Please ask me, if you are interested!

Acknowledgements and references

- Collaborators
  - Chris-Kriton Skylaris (Southampton)
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  - Narbe Mardirossian (Berkeley)
- Compute resources
  - University of Southampton
    IRIDIS HPC facility
- Software
  - ONETEP (www.onetep.org)
  - Q-Chem (www.q-chem.com)
- References
  - J.C. Womack, N. Mardirossian, M. Head-Gordon, and C.-K. Skylaris, J. Chem. Phys. **145**, 204114 (2016)
  - N. Mardirossian, L. Ruiz Pestana, J.C. Womack, C.-K. Skylaris, T. Head-Gordon, and M. Head-Gordon, J. Phys. Chem. Lett. **8**, 35 (2017)

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