

Supplementary material for the article

## Self-consistent implementation of meta-GGA functionals for the ONETEP linear-scaling electronic structure package

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### I. COMPUTATIONAL DETAILS

#### A. Structures

All the molecular geometry data used to obtain the results presented in the paper is provided in text files, separate to this document. The geometries of the molecules used in the binding energy and conformation energy calculations are provided in XYZ format, in units of angstrom. The structures of the amyloid fibril segments used in the computational scaling calculations are provided in ONETEP input format, in units of bohr. Bibliographic information is provided in additional text files associated with the geometry data.

#### B. Pseudopotentials

All ONETEP calculations were performed using norm-conserving pseudopotentials. The binding energy and conformation energy calculations used pseudopotentials from the Rappe-Bennett pseudopotential library (GGA-optimized) [1] for H, C, N, O and F nuclei [2]. The OPIUM pseudopotential generator [3] was used to generate the pseudopotential for S, used in calculations on cysteine [4]. The pseudopotential files used in the binding and conformation energy calculations are provided in ONETEP-compatible format, separate to this document.

### II. ADDITIONAL RESULTS

#### 1. B97M-V and B97M-rV

To investigate the effect of replacing the original VV10 non-local correlation (NLC) functional [5] with revised VV10 NLC [6] in B97M-V [7], the Q-Chem calculations reported in the paper were performed using B97M-V and B97M-rV, where the “V” and “rV” suffixes indicate use of original and revised VV10 NLC, respectively. In the paper, the B97M-rV results were used for comparisons with ONETEP, since only the revised VV10 NLC functional is available in ONETEP. The results of these B97M-V and B97M-rV calculations for all the binding energy and conformation energy systems used in of the paper are presented in Table S1.

The results presented in Table S1 were performed using a development version of Q-Chem 4 [8], and used the def2-QZVPPD basis set for all atoms [9, 10]. The (99,590) integration grid (99 radial shells per atom, 590 angular grid points per shell) was used to evaluate the local part of B97M-V and B97M-rV and the SG-1 grid [11] was used to evaluate the NLC component of the functionals.

B97M-V and B97M-rV used the same parameters for the local and NLC parts of the functionals. The parameters for the local part of the functional were optimized for the original VV10 NLC functional, with parameters  $b = 6.0$  and  $C = 0.01$ . We expect B97M-rV to behave slightly differently when the same  $b$  and  $C$  parameters are used for rVV10 NLC, based on the differences between the VV10 and rVV10 functionals described in Ref. 6. This is observed in Table S1, where the difference between B97M-V and B97M-rV was typically less than  $0.1 \text{ kcal mol}^{-1}$ , with somewhat larger differences of  $0.240$  and  $0.151 \text{ kcal mol}^{-1}$  for the binding energy of  $\text{C}_6\text{H}_6 \cdots \text{C}_6\text{H}_3\text{F}_3$  and relative energy of the “dw” conformer of melatonin, respectively.

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Sabatini and coworkers compared the VV10 and rVV10 functionals (local and NLC components) using the  $b = 5.9$  and  $C = 0.0093$  parameters obtained for the original functional (see the supplementary information for Ref. 6) for calculating binding energies of complexes in the S22 set [12]. The authors found that rVV10 with the original  $b$  and  $C$  values typically produced a small increase in binding energy, typically a fraction of a kcal mol<sup>-1</sup>. The largest difference seen for the S22 set was 0.85 kcal mol<sup>-1</sup> and by reoptimizing the  $b$  parameter for rVV10 (to give  $b = 6.3$ ), Sabatini and coworkers reduced the maximum difference to 0.16 kcal mol<sup>-1</sup>.

We observe the same overbinding effect, though to a smaller extent, with B97M-rV, where all binding energies calculated using rVV10 NLC were slightly larger than those using original VV10 NLC. Based on the results of Sabatini and coworkers, we suspect that reoptimization of the local and/or non-local parameters of B97M-rV would reduce the already small disagreement between the two versions of the functional.

The difference between B97M-V and B97M-rV does not directly bear on the comparisons between ONETEP and Q-Chem energies presented in the paper, since these results were produced using B97M-rV only. However, for users of either variant of the functional, it is useful to note that B97M-rV (without reoptimization of parameters) can be expected to give slightly different results to B97M-V.

TABLE S1. Comparison of binding and conformation energies, in kcal mol<sup>-1</sup>, calculated using Q-Chem with the B97M-V and B97M-rV functionals. The differences between energies calculated using the B97M-V and B97M-rV functionals are listed in the column labeled  $\Delta$ . RMSDs for the binding energies and conformation energies are reported below the  $\Delta$  column. Binding energies are without corrections for basis set superposition error and with monomer geometries derived from the complex. Conformer energies are calculated relative to the lowest energy conformer in each case: “I” for cysteine and “aa” for melatonin. For additional computational details, see section II 1.

		B97M-V	B97M-rV	$\Delta$
Binding energies				
CH <sub>3</sub> F...CH <sub>3</sub> F		-1.402	-1.435	-0.033
C <sub>6</sub> H <sub>6</sub> ...C <sub>6</sub> H <sub>3</sub> F <sub>3</sub>		-4.268	-4.508	-0.240
C <sub>6</sub> H <sub>6</sub> ...H <sub>2</sub> O (I)		-1.190	-1.214	-0.024
C <sub>6</sub> H <sub>6</sub> ...H <sub>2</sub> O (II)		-3.206	-3.283	-0.077
		RMSD		0.128
Conformation energies				
Cysteine	II	1.460	1.481	0.020
Cysteine	III	1.322	1.313	-0.008
Cysteine	IV	1.492	1.481	-0.011
Melatonin	be	5.541	5.582	0.041
Melatonin	dw	9.274	9.424	0.151
		RMSD		0.071

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- [3] Opium pseudopotential generation project, <http://opium.sourceforge.net/>.
- [4] This pseudopotential is part of a suite of norm-conserving pseudopotentials generated by K. Refson to supplement the Rappe-Bennett library, available to download from the CASTEP project page on CCPForge: <https://ccpforge.cse.rl.ac.uk/gf/project/castep/>.
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