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**Validation Challenge of Density-Functional Theory for Peptides:  
Example of Ac-Phe-Ala<sub>5</sub>-LysH<sup>+</sup>** VOLKER BLUM<sup>1</sup>, MARIANA ROSSI<sup>2</sup>, SUCISMITA CHUTIA, MATTHIAS SCHEFFLER, Fritz Haber Institute, Berlin, Germany — We assess the performance of a group of exchange-correlation functionals for predicting the secondary structure of peptide chains, up to a new many-body dispersion corrected hybrid density functional, coined PBE0+MBD\*. For the purpose of validation, we first compare to published, high-level CCSD(T) benchmark conformational energy hierarchies for 73 conformers of small three-residue peptides, establishing that the van der Waals corrected PBE0 functional yields an average error of only  $\approx 20$  meV ( $\approx 0.5$  kcal/mol). This compares to  $\approx 40$ -50 meV for non-dispersion corrected PBE0 and 50-100 meV for different empirical force fields. For longer peptide chains that form secondary structure, CCSD(T) level benchmark data are currently unaffordable. We thus turn to the experimentally well studied Ac-Phe-Ala<sub>5</sub>-LysH<sup>+</sup> peptide, for which four closely competing conformers were experimentally established. For comparison, an exhaustive conformational space exploration yields at least eleven competing low energy minima. We show that (i) the many-body dispersion correction, (ii) the hybrid functional nature of PBE0+MBD\*, and (iii) zero-point corrections are needed to reveal the four experimentally observed structures as the minima that would be populated at low temperature.

<sup>1</sup>Present address: Center for Materials Genomics, Duke University, USA

<sup>2</sup>Current address: Chemistry Department, University of Oxford, UK

Mariana Rossi  
Chemistry Department, University of Oxford

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