

Abstract Submitted  
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**How van der Waals interactions affect alanine-based polypeptides** M. ROSSI, V. BLUM, X. REN, A. TKATCHENKO, M. SCHEFFLER, Fritz-Haber-Institut, Berlin — van der Waals interactions play a critical role among the intramolecular interactions that stabilize secondary structure folding motifs in polypeptides. In this work, we quantify its influence *ab initio* for the series of helix-forming alanine based polypeptides Ac-Ala<sub>n</sub>-LysH<sup>+</sup> ( $n = 4-15$ ). We show that: (i) applying a van der Waals (vdW) correction based on the self-consistent electron density [2] to the PBE functional, a clear  $\alpha$ -helical conformational preference emerges at  $n=8$ , in agreement with experiment [1], while a mostly  $3_{10}$  helical structure is preferred at plain PBE; (ii) a numeric atom-centered orbital basis enhanced specifically to converge conformational energy differences from explicitly correlated methods (MP2, EX+cRPA and beyond [3]) gives us benchmark capabilities for treatments that include long-range correlations outrightly; (iii) exploring the free energy surface through *ab initio* dynamics for longer helices ( $n=15$ ) we see a dramatic influence of vdW interactions for high temperature stability and surface explored by these molecules. Our results demonstrate that we are now in a position to quantify vdW contributions accurately, and thus unravel their critical qualitative role in comparison to other contributions (strain, H-bonds) in medium-sized biomolecules. [1] Kohtani and Jarrold, JACS 108, 8454 (2004); [2] Tkatchenko and Scheffler, PRL 102, 073055 (2009); [3] <http://www.fhi-berlin.mpg.de/aims>

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