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**Finite size effect on hydrogen bond cooperativity in  $(\text{Ala})_n$  polypeptides: A DFT study using numeric atom-centered orbitals** VOLKER BLUM, Fritz-Haber-Institut, JOEL IRETA, MATTHIAS SCHEFFLER — An accurate representation of the energetic contribution  $E_{\text{hb}}$  of hydrogen bonds to structure formation is paramount to understand the secondary structure stability of proteins, both qualitatively and quantitatively. However,  $E_{\text{hb}}$  depends strongly on its environment, and even on the surrounding peptide conformation itself. For instance, a short  $\alpha$ -helical polypeptide  $(\text{Ala})_4$  can not be stabilized by its single hydrogen bond, whereas an infinite  $\alpha$ -helical chain  $(\text{Ala})_\infty$  is clearly energetically stable over a fully extended conformation. We here use all-electron density functional calculations in the PBE generalized gradient approximation by a recently developed, computationally efficient numeric atom-centered orbital based code<sup>1</sup> to investigate this H-bond *cooperativity* that is *intrinsic* to Alanine-based polypeptides  $(\text{Ala})_n$  ( $n=1-20,\infty$ ). We compare finite and infinite prototypical helical conformations ( $\alpha$ ,  $\pi$ ,  $3_{10}$ ) on equal footing, with both neutral and ionic termination for finite  $(\text{Ala})_n$  peptides. Moderately sized NAO basis sets allow to capture  $E_{\text{hb}}$  with meV accuracy, revealing a clear jump in  $E_{\text{hb}}$  (cooperativity) when two H-bonds first appear in line, followed by slower and more continuous increase of  $E_{\text{hb}}$  towards  $n \rightarrow \infty$ . <sup>1</sup> V. Blum, R. Gehrke, P. Havu, V. Havu, M. Scheffler, *The FHI Ab Initio Molecular Simulations (aims) Project*, Fritz-Haber-Institut, Berlin (2006).

Prefer Oral Session  
 Prefer Poster Session

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