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Finite size effect on hydrogen bond cooperativity in $(Ala)_n$ polypeptides: A DFT study using numeric atom-centered orbitals
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— An accurate representation of the energetic contribution $E_{\rm hb}$ of hydrogen bonds to structure formation is paramount to understand the secondary structure stability of proteins, both qualitatively and quantitatively. However, $E_{\rm hb}$ depends strongly on its environment, and even on the surrounding peptide conformation itself. For instance, a short α-helical polypeptide $(Ala)_4$ can not be stabilized by its single hydrogen bond, whereas an infinite α-helical chain $(Ala)_\infty$ 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[1] to investigate this H-bond *cooperativity* that is *intrinsic* to Alanine-based polypeptides $(Ala)_n$ (n=1-20,∞). We compare finite and infinite prototypical helical conformations (α, π, 3_{10}) on equal footing, with both neutral and ionic termination for finite $(Ala)_n$ peptides. Moderately sized NAO basis sets allow to capture $E_{\rm hb}$ with meV accuracy, revealing a clear jump in $E_{\rm hb}$ (cooperativity) when two H-bonds first appear in line, followed by slower and more continuous increase of $E_{\rm hb}$ towards $n \to \infty$.
[1] V. Blum, R. Gehrke, P. Havu, V. Havu, M. Scheffler, *The FHI Ab Initio Molecular Simulations (aims) Project*, Fritz-Haber-Institut, Berlin (2006).

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