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 \textit{ab initio} for the series of helix-forming alanine based polypeptides Ac-Ala$_n$-LysH$^+$ ($n = 4$-$15$). We show that: (i) applying a van der Waals (vdW) correction based on the self-consistent electron density \cite{Tkatchenko2009} to the PBE functional, a clear $\alpha$-helical conformational preference emerges at $n=8$, in agreement with experiment \cite{Kohtani2004}, 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 \cite{Aims}) gives us benchmark capabilities for treatments that include long-range correlations outrightly; (iii) exploring the free energy surface through \textit{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. \cite{Kohtani2004, Tkatchenko2009, Aims}

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