Diffusion Monte Carlo applied to weak interactions - hydrogen bonding and aromatic stacking in (bio-)molecular model systems M. FUCHS, J. IRETA, M. SCHEFFLER, Fritz-Haber-Institut der MPG, Berlin, C. FILIPPI, Instituut Lorentz, Univ. Leiden — Dispersion (Van der Waals) forces are important in many molecular phenomena such as self-assembly of molecular crystals or peptide folding. Calculating this nonlocal correlation effect requires accurate electronic structure methods. Usual density-functional theory with generalized gradient functionals (GGA-DFT) fails unless empirical corrections are added that still need extensive validation. Quantum chemical methods like MP2 and coupled cluster are more accurate, yet limited to rather small systems by their unfavorable computational scaling. Diffusion Monte Carlo (DMC) can provide accurate molecular total energies and remains feasible also for larger systems. Here we apply the fixed-node DMC method to (bio-)molecular model systems where dispersion forces are significant: (dimethyl-) formamide and benzene dimers, and adenine-thymine DNA base pairs. Our DMC binding energies agree well with data from coupled cluster (CCSD(T)), in particular for stacked geometries where GGA-DFT fails qualitatively and MP2 predicts too strong binding.

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