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The quantum nature of the hydrogen bond: insight from path-integral molecular dynamics BRENT WALKER, XIN-ZHENG LI, ANGELOS MICHAELIDES, London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, U.K — Hydrogen (H) bonds are weak, generally intermolecular bonds, that hold together much of soft matter, the condensed phases of water, network liquids, and many ferroelectric crystals. The small mass of H means H-bonds are inherently quantum mechanical; effects such as zero point motion and tunneling should be considered, although often are not. In particular, a consistent picture of quantum nuclear effects on the strength of H-bonds and consequently the structure of H-bonded systems is still absent. Here, we report *ab initio* path-integral molecular dynamics studies on the quantum nature of the H-bond. Systematic examination of a range of H-bonded systems shows that quantum nuclei weaken weak H-bonds but strengthen relatively strong ones. This correlation arises from a competition between anharmonic intermolecular bond bending and intramolecular bond stretching. A simple rule of thumb enables predictions to be made for H-bonded bonded materials in general with merely classical knowledge (e.g. H-bond strength or H-bond length). Our work rationalizes the contrasting influence of quantum nuclear dynamics on a wide variety of materials, including liquid water and HF, and highlights the need for flexible molecules in force-field based studies of quantum nuclear dynamics.

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