# The quantum nature of the proton in water-hydroxyl overlayers on metal surfaces

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The first layer of water on many surfaces is comprised of mixed arrangements of water and hydroxyl molecules. We show here with an ab initio approach (density-functional theory in conjunction with path-integral molecular dynamics) that such overlayers on transition metal surfaces exhibit pronounced quantum nuclear effects. The metal substrates serve to reduce the classical proton transfer barriers within the overlayers and, in analogy to ice under high pressure, to shorten the corresponding intermolecular hydrogen bonds.

Depending on the substrate and the intermolecular distance it imposes on the overlayer, the traditional distinction between covalent and hydrogen bonds within the overlayers is lost partially (e.g. on Pt(111)) or almost entirely (e.g. on Ni(111)). This, in turn, has a marked effect on the oxygen sublattice.

The key implications of this work are:

(i) quantum nuclear effects have a profound impact on the nature and structure of the hydrogen bond at interfaces and should therefore not be overlooked;

(ii) a platform on which the magnitude of quantum nuclear effects in hydrogen bonds can be systematically tuned and probed experimentally and theoretically has been identified.

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