# The Role of Quantum Effects on Structural and Electronic Fluctuations in Neat and Charged Water

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# Clustering Algorithm

As indicated in the main text, for constructing the connectivity of the graph, we used a cutoff of $|\nu| < 0.2$Å. Here we show the results obtained for Figure 1 and Figure 2 in the main manuscript using a larger and smaller cutoff. When we use a cutoff of $|\nu| < 0.15$Å, this imposes a stricter restriction on a particular proton to be classified as shared along a hydrogen bond. In the context of the CP simulations for example, this means that the proportion of species identified as Eigen-like increases while those considered as Zundel reduces. However, we observe that there is still a significant probability for the excess proton to delocalize over several water molecules relative to what is seen in the classical simulations. Furthermore, comparing the CW and QW simulations, the correlated motion of protons across several hydrogen bonds also shows that quantum fluctuations lead to rather drastic transient autoionization events. The same holds for the choice of using a large cutoff where $|\nu| < 0.25$Å. The figures below show the results obtained for Figure 1 and 2 in the manuscript for the smaller and larger cutoffs.

# Hydrogen bond correlations

As indicated in the main text, the joint probability distributions $P(\nu_A, \nu_B)$ change quite significantly as a function of distance from the center of charge. Close to the center of charge there are very large correlations between different hydrogen bonds indicative of the correlated or concerted nature of the proton transfer events going on in the hydrogen bond network. Below we show the joint probability distributions at different distances from the center of charge for the classical (Figure 5) and quantum (Figure 6) proton.

As in the case of neutral water, a strong component of the joint probability distribution is just the product of the distribution for an individual bond. For instance, at very short distances $d = 0.5$Å, the configuration is probably Eigen-like, with a much larger probability of having a donated bond – to the point that the probability of finding two donated bonds is much larger than the probability of finding one donated and one accepted bond. Cross-correlations are very strong, as a consequence of both the highly concerted motion of protons in the vicinity of the excess charge, and of the slight ambiguity in the definition of the center of charge. For instance, at $d = 0.5$Å there is a negligible probability of finding a weak donated bond: the Eigen cation donates very strong, delocalized H-bonds. The presence of a weakly donated bond signals the fact that the cluster is probably not Eigen-like, but a symmetric configuration involving three water molecules and two symmetric, shared protons. In this configuration, the central O atom is less hydrophobic, so there is a dramatic increase in the probability of accepting a HB. Were not for the poor statistics, it would be interesting to separate the contributions from different kinds of charged clusters, to have a clearer picture of the interplay between "local" correlations around a O atom and the long-range correlations in the HB network. Configurations with $d \geq 2.5$ approach the distributions observed in bulk, neat water, however with a much increased degree of delocalization.

The quantum distributions (Figure 6) are to a large extent analogous to the classical ones, with a

much increased overall spread of the peaks in the distribution, and a softening of the correlations. This is a manifestation of the fact that quantum fluctuations take place on a very local scale, on top of a long-range structure of the HB network that it mostly determined at the classical level. The interplay between the two aspects, however, mean that – just like in the case of neutral water – correlated motion across the network is much more statistically relevant in the quantum case than with a classical description of the nuclei.

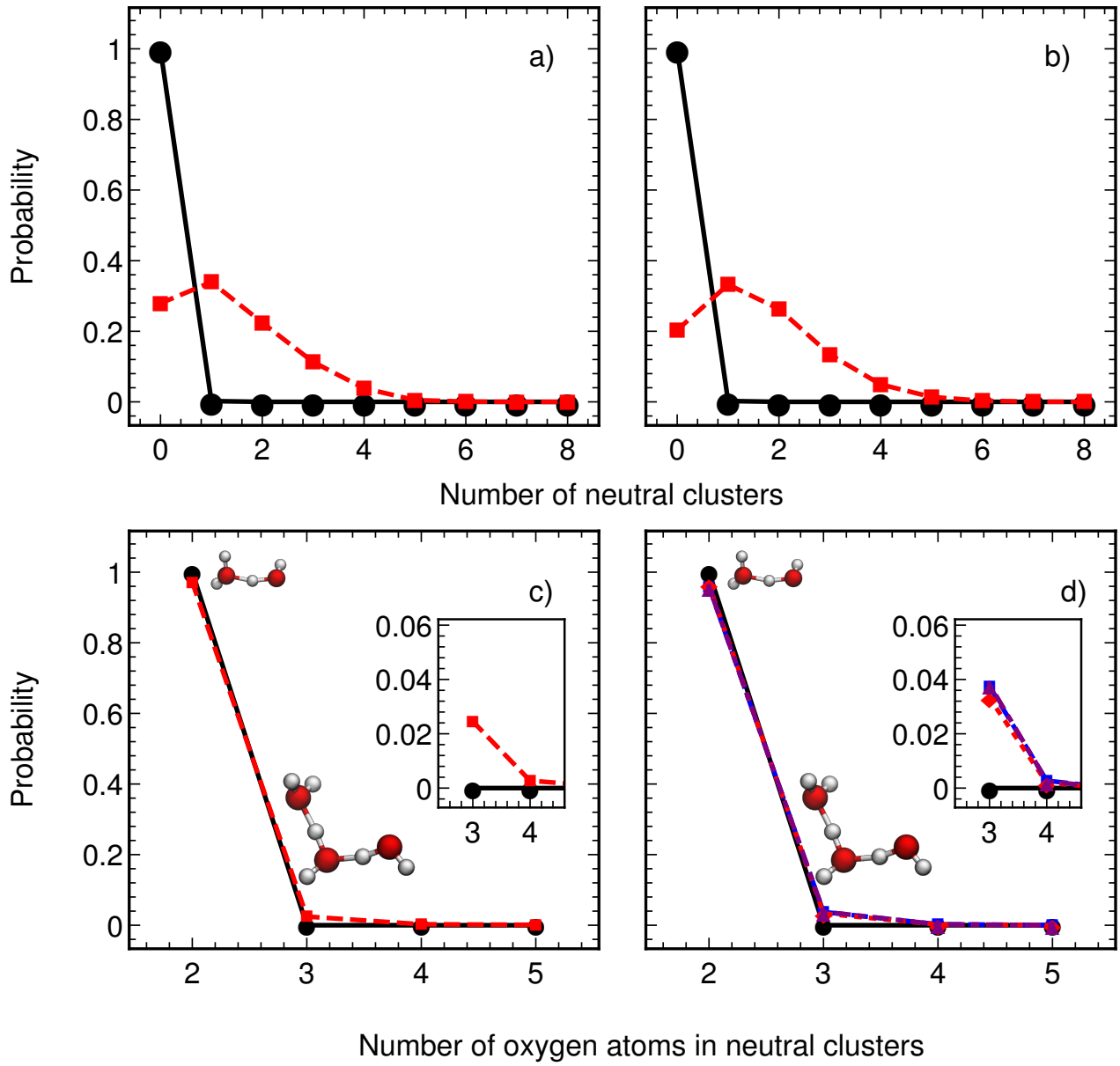


Figure 1: Same as Figure 1 in the main text but using a cutoff of 0.15 to construct the graph as describe in the text above.

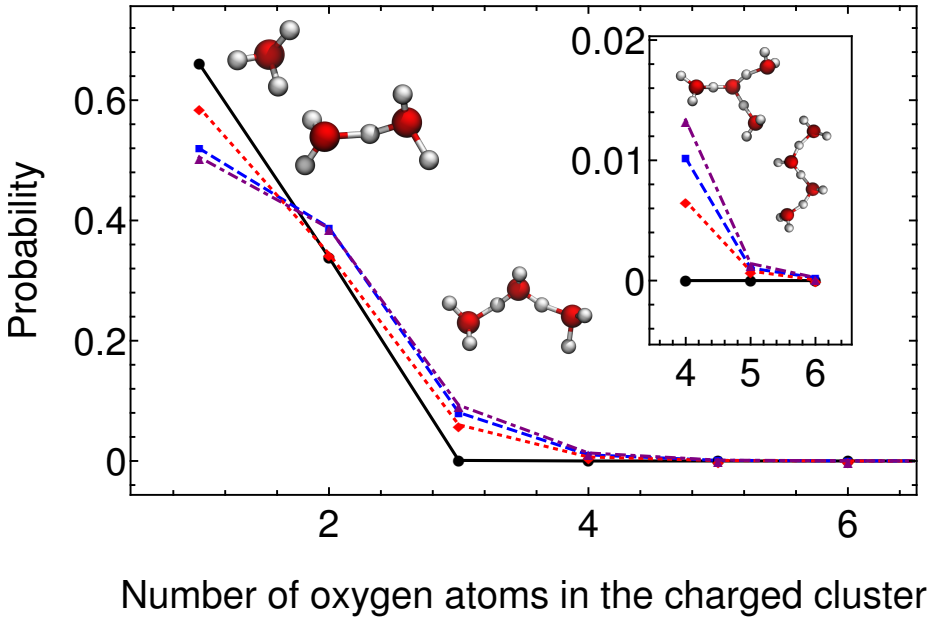


Figure 2: Same as Figure 2 in the main text but using a cutoff of 0.15 to construct the graph as described in the text above.

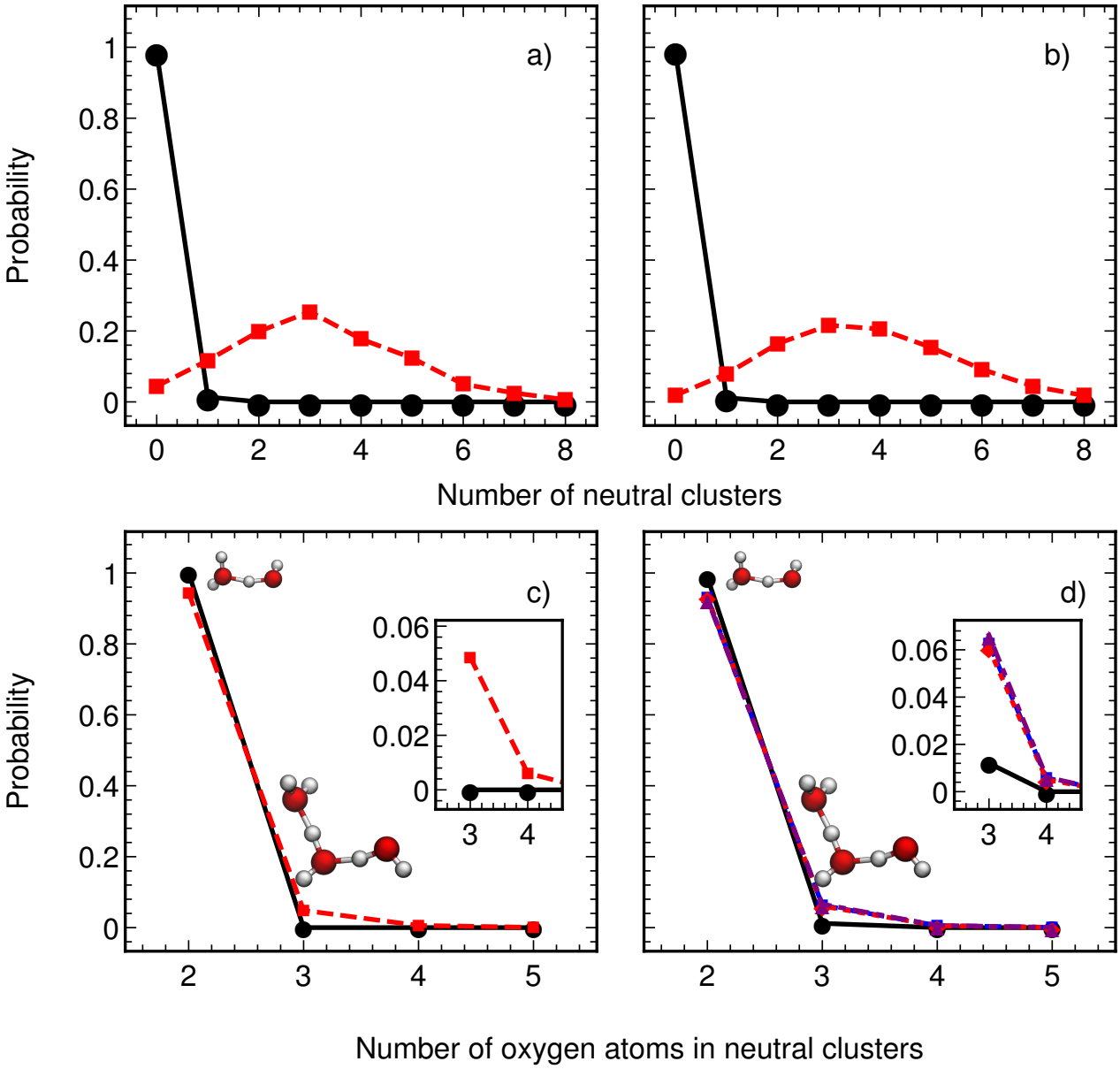


Figure 3: Same as Figure 1 in the main text but using a cutoff of 0.25 to construct the graph as describe in the text above.

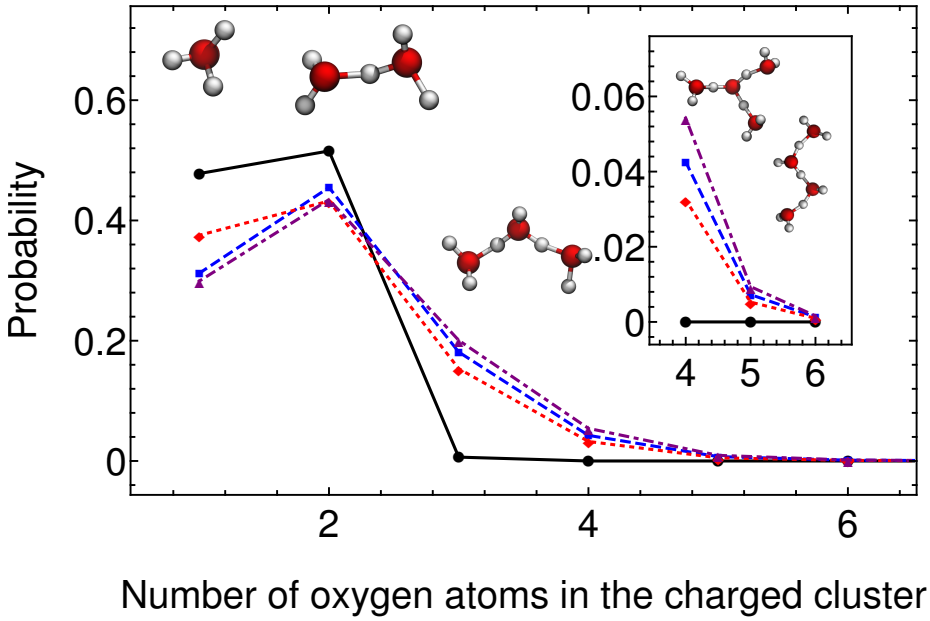


Figure 4: Same as Figure 2 in the main text but using a cutoff of 0.25 to construct the graph as described in the text above.

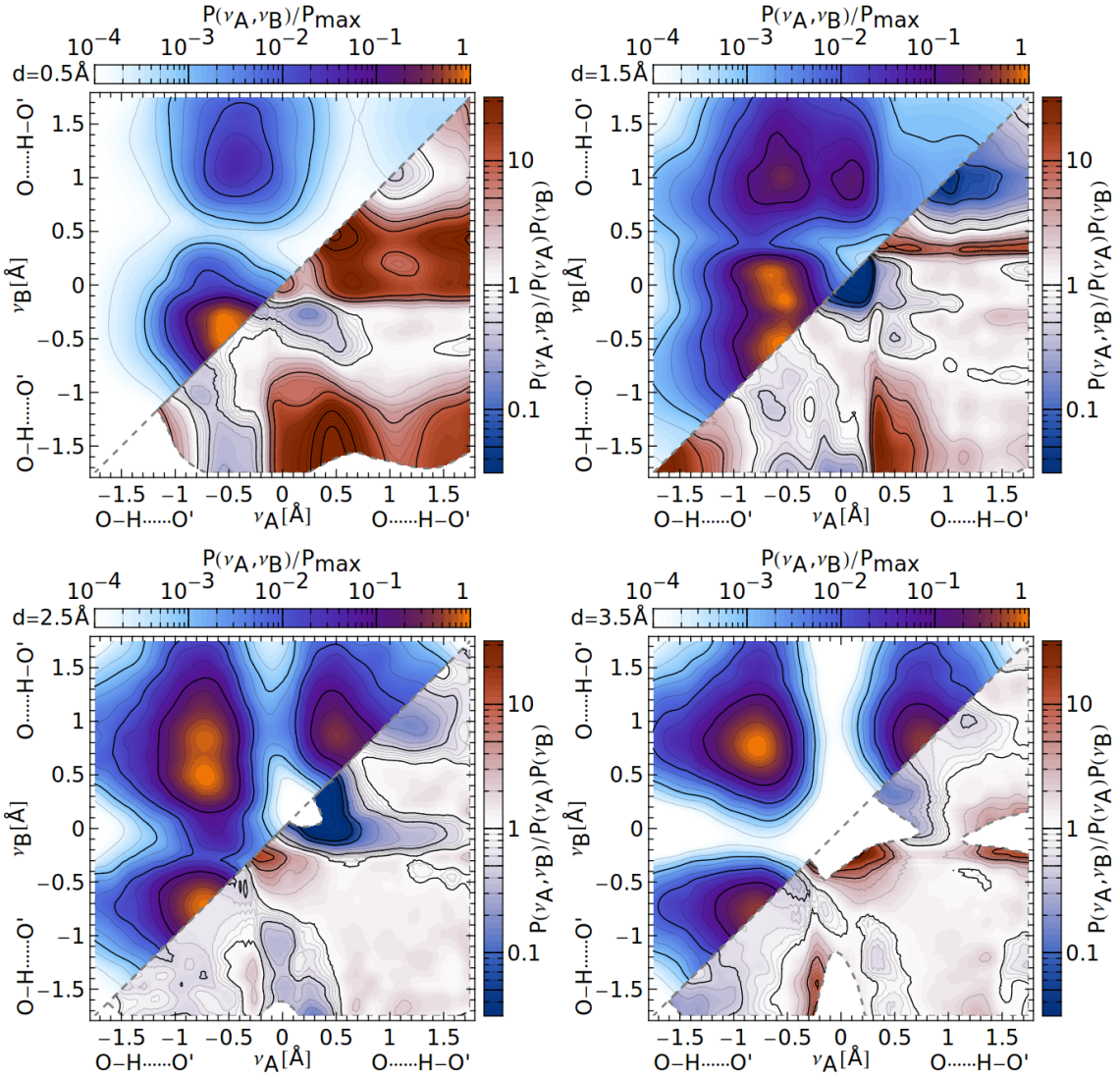


Figure 5: Joint probability distribution of two hydrogen bonds sharing the same oxygen atom O, as a function of the distance $d$ between O and the center of charge, for an *ab initio* classical simulation of liquid water at 300K. The four panels show slices of $P(\nu_A, \nu_B, d)/P(d)$ for $d = 0.5$, $d = 1.5$, $d = 2.5$, and $d = 3.5$Å. The upper left corners show the joint probability and the lower right corners, instead, show the ratio between the joint probability and the product of the marginals.

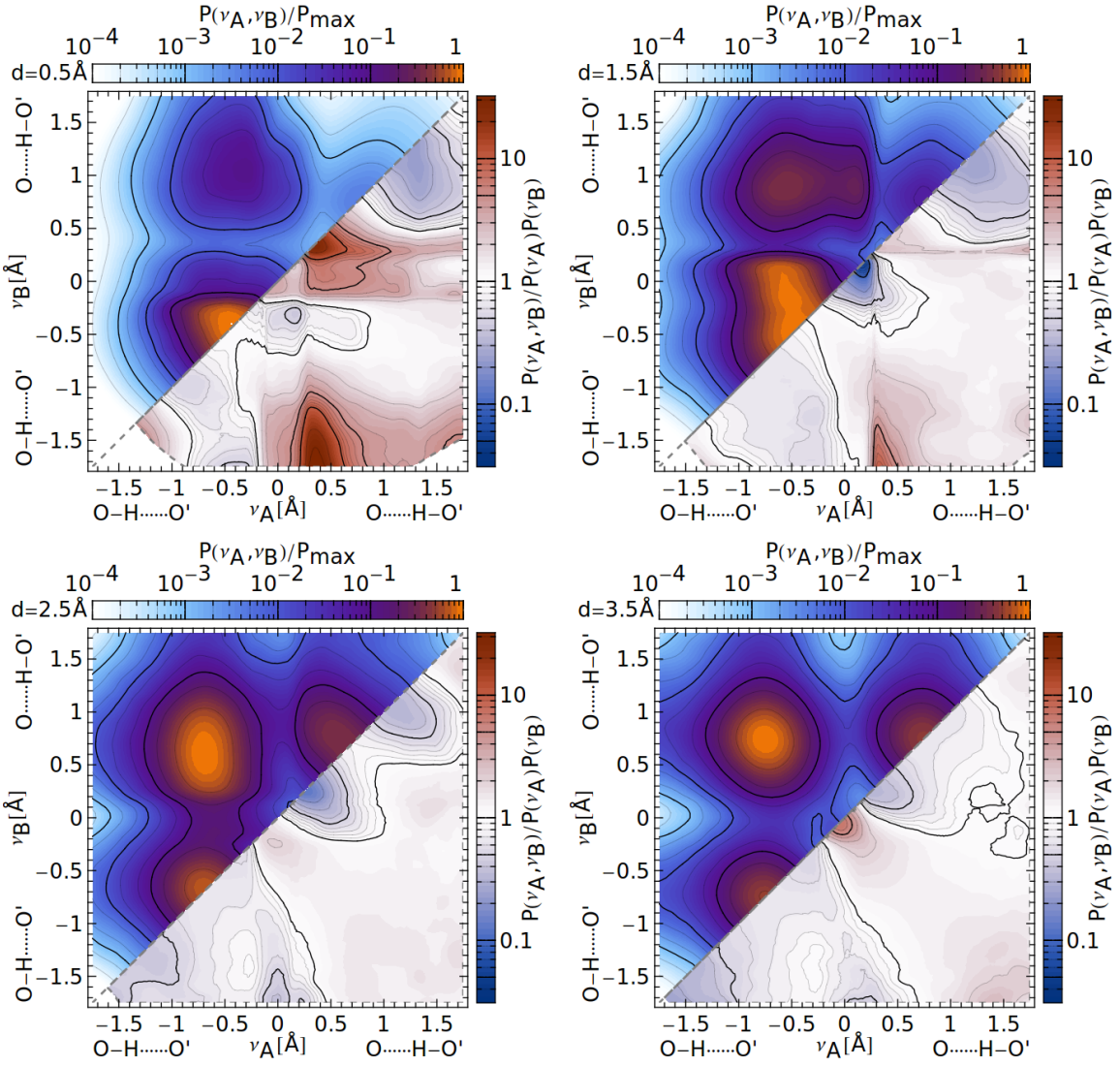


Figure 6: Joint probability distribution of two hydrogen bonds sharing the same oxygen atom O, as a function of the distance $d$ between O and the center of charge, for an *ab initio* quantum simulation of liquid water at 300K. The four panels show slices of $P(\nu_A, \nu_B, d)/P(d)$ for $d = 0.5$, $d = 1.5$, $d = 2.5$, and $d = 3.5$Å. The upper left corners show the joint probability and the lower right corners, instead, show the ratio between the joint probability and the product of the marginals.