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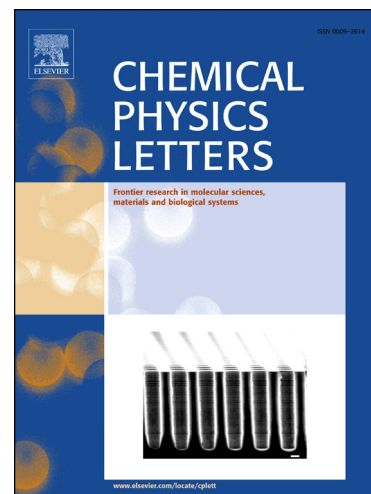
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Unravelling the influence of quantum proton delocalization on electronic charge transfer through the hydrogen bond

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Upon hydrogen bond formation, electronic charge density is transferred between the donor and acceptor, impacting processes ranging from hydration to spectroscopy. Here we use ab initio path integral simulations to elucidate the role of nuclear quantum effects in determining the charge transfer in a range of hydrogen bonded species in the gas and liquid phase. We show that the quantization of the nuclei gives rise to large changes in the magnitude of the charge transfer as well as its temperature dependence. We then explain how a single geometric parameter determines the charge transfer through the hydrogen bond. These results thus demonstrate that nuclear quantum effects are vital for the accurate description of charge transfer and offer a physically transparent way to understand how hydrogen bonding gives rise to it.

Keywords: charge transfer, nuclear quantum effects, hydrogen bonding

I. INTRODUCTION

The transfer of electronic charge density through a hydrogen bond manifests in effects ranging from the stabilization and spectroscopy of hydrated ions and aqueous solutions^{1–4} to the charging of polar residues in proteins⁵, and has even been implicated in explaining the observed zeta potential at hydrophobic interfaces^{2,6,7}. However, defining the amount of charge transfer (CT) remains a subject of significant debate, since partitioning the electron density and assigning it to particular atoms or molecules is not uniquely defined. This has led to the introduction of a number of approaches to calculate the charge transfer and charge transfer energy, with different approaches exhibiting both different quantitative and qualitative behavior^{8–16}. For example, methods based on natural bond orbitals suggest that without CT the 0 K water dimer would adopt a different structure^{17,18}. However, studies using other methods suggest a much less substantial role of CT in stabilizing the water dimer hydrogen bond^{19–22}.

Previous CT studies of hydrogen bonded systems have analyzed minimum energy structures^{18–20} or those obtained from simulations that treat the nuclei classically^{7,23}. However, nuclear quantum effects (NQE), such as zero-point energy and tunnelling, are known to significantly change the geometry of hydrogen bonded systems^{24–29}. The zero-point energy along the hydrogen bond increases the ability of the proton to delocalize between the donor and acceptor, resulting in shorter and stronger hydrogen bonds. On the other hand, the distortion of the hydrogen bond due to quantization of the librational modes perpendicular to the hydrogen bond

leads to weaker hydrogen bonding. The relative importance of these two competing quantum effects³⁰ leads to cases where NQEs strengthen³¹ or weaken³² hydrogen bonds, depending on the geometry and chemical environment. This competition has been used to elucidate the seemingly anomalously small NQEs and resulting isotope effects observed in many systems³³.

Here we investigate the role of NQEs in modulating the CT characteristics of a range of hydrogen bonded systems involving water and ions in both the gas and condensed phase and show how these can be understood based on the changes in the hydrogen bond geometry. We demonstrate that NQEs give rise to large changes in both the amount of CT and its contribution to the donor-acceptor interaction energy, independent of the method used to study charge transfer. In particular, including NQEs increases CT in some cases, while decreasing it in others. It also leads to a much milder temperature dependence of CT in all cases. To uncover the reasons for this, we show that the amount of charge transfer is almost exclusively determined by a scaled proton sharing coordinate. We use this observation to demonstrate that the charge of a water molecule in liquid water can be accurately estimated from the values of this coordinate for each hydrogen bond the molecule forms, thus provides a straightforward approach to modelling CT in solution.

II. SIMULATION DETAILS

To evaluate NQEs on electronic properties in the gas phase, 20 ps ab initio path integral molecular dynamics (AI-PIMD) simulations at 25 K and 300 K of the water dimer as well as the water-fluoride and water-iodide complex were performed. These simulations were performed with a time step of 0.5 fs with 256 and 32 replicas, at the two respective temperatures. The B3LYP^{34,35} exchange

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