

Name: Peer Review Information for "Nuclear Quantum Effects on the Electronic Structure of Water and Ice"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

The authors report a comprehensive study of on the role of quantum nuclear effects on band gap renormalization of water and ice estimated with many body perturbation theory. They use converged system sized, simulation lengths and properly accounted for anharmonic motion at finite temperature. To estimate the range of uncertainty from modeling they reported results obtained from using multiple potential energy surfaces and electronic structure methods. Finally they report a clear correlation between proton delocalization and electronic localisation.

The paper is well done with careful benchmarks. I recommend publication after minor corrections

Important

1. The authors use the phrase "nuclear quantum dynamics" or "quantum dynamics" across the paper. It would be better to rephrase them to "(nuclear) quantum effects" as the effects being referred to in this work are steady state fluctuations rather than arising from quantum mechanical temporal dynamics. This distinction becomes even more important when the authors discuss results from the PIGLET thermostat, which doesn't even approximate true quantum dynamics.
2. The authors may want to refer to <https://doi.org/10.1021/acs.jctc.9b00596> when referring to the inaccuracy of the self consistent field approach due to improper modeling of large amplitude curvilinear motion.
3. Unfortunately, PIGLET 8 replicas is known to overestimate the proton transfer coordinate. See Fig 5 of <https://doi.org/10.1063/1.4971438>. The authors should either redo the calculations with 32 or

64 replicas or include a benchmark at one level of theory to ensure that the effect of quantum nuclear motion on the band gap isn't overestimated.

4. "proton delocalization, and the resulting enhanced transient autoprotolysis, observed in PIMD simulations are the main cause for the much larger nuclear quantum effects on the bandgap renormalization of ice Ih, compared to water."

The authors can rephrase this as a correlation rather than a causation.

Minor

5. The authors can explicitly state that the architecture (NEP) of the revpbe0-D3 potential when first referenced as they have for the SCAN potential.

6. Why isn't 77 K a more relevant condition to study ice given the existence of experimental results? Wouldn't the results be expected to be different considering a lower probability of proton transfer?

7. How do the authors account for proton disorder in ice Ih? This could be easily checked as meta GGA level.

8. The phrase "bandgap renormalization of 1.65 eV due to NQEs using a geometry-optimized structure " is confusing. Can the authors clarify?

9. It would be good to elaborate a bit more on this point "The underestimation of the bandgap with revPBE0 can be in

part attributed to the fact that the inverse of the appropriate fraction of exact exchange (α) in the hybrid functional is more than two times larger than that of the electronic dielectric constant (ϵ_∞) of water."

10. Fig 2 could be made more clear by using dashed lines for classical Vs quantum and just two colours.

11. Hydrogen bonds can strengthen due to proton sharing as opposed to how is discussed in "may also stem from the weakening of hydrogen bonds due to quantum delocalization"

12. Can the authors clarify the definition of the proton transfer coordinate? The way it's defined currently, it can't have positive values. However, Fig 3 has positive values.

Author's Response to Peer Review Comments:

Dear Editor,

thank you for handling our manuscript. We have addressed all the reviewers' comments and the editorial requests.

Please see the attached resubmission letter.

Sincerely

Davide Donadio

Dear Editor,

We thank the reviewer for their insightful comments. We have addressed all the issues raised by the reviewers and we have modified the manuscript accordingly. Please, consider the revised manuscript "Nuclear Quantum Effects on the Electronic Structure of Water and Ice". We have submitted a copy of the manuscript where changes are highlighted in blue.

We hereby address the comments from Referee 1:

1) *The authors use the phrase "nuclear quantum dynamics" or "quantum dynamics" across the paper. It would be better to rephrase them to "(nuclear) quantum effects" as the effects being referred to in this work are steady state fluctuations rather than arising from quantum mechanical temporal dynamics. This distinction becomes even more important when the authors discuss results from the PIGLET thermostat, which doesn't even approximate true quantum dynamics.*

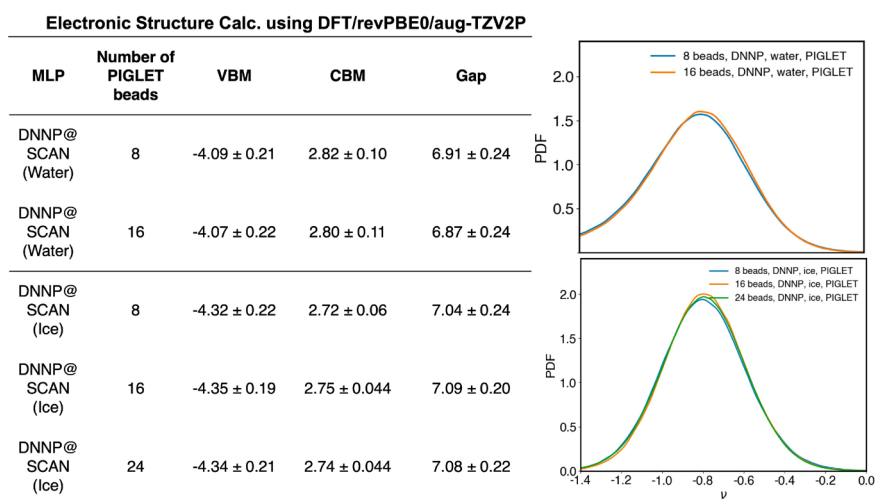
We agree with the reviewer that it is more appropriate to rephrase "nuclear quantum dynamics" as "nuclear quantum effects" and we have made the appropriate changes in the manuscript.

2) *The authors may want to refer to <https://doi.org/10.1021/acs.jctc.9b00596> when referring to the inaccuracy of the self-consistent field approach due to improper modeling of large amplitude curvilinear motion.*

We thank the reviewer for suggesting this article. We have included the reference in the main text (reference number 36), in the discussion of stochastic methods based on the quasi-harmonic approximation.

3) Unfortunately, PIGLET 8 replicas is known to overestimate the proton transfer coordinate. See Fig 5 of <https://doi.org/10.1063/1.4971438>. The authors should either redo the calculations with 32 or 64 replicas or include a benchmark at one level of theory to ensure that the effect of quantum nuclear motion on the band gap isn't overestimated.

We thank the reviewer for pointing this out. We carried out convergence tests on the band gap and proton transfer coordinate distribution for PIGLET with 16 beads for water and for 16 and 24 beads for ice (as with i-PI the maximum number of beads that can be run with PIGLET is 24). The results of the convergence test using the SCAN-based DeepMD model are reported in Table S1: We see that for both ice at 230 K



and water at 300 K the band gap with 8 beads is converged within 50 meV of that computed with 16-bead runs. We have included this convergence test in the SI. During careful rechecking of our data, we found that in our earlier version of the manuscript, only for PIGLET/NEP simulation of ice, incorrect GLE matrices were used. We have corrected this discrepancy in this version and provided the updated figures accordingly. The bandgap renormalization of ice due to NQE is reduced to 1.2 eV from the former 1.5 eV, bringing the two MLP models in better agreement. These changes do not affect the original conclusions of the manuscript.

4) “proton delocalization, and the resulting enhanced transient autoprotolysis, observed in PIMD simulations are the main cause for the much larger nuclear quantum effects on the bandgap renormalization of ice Ih, compared to water.” The authors can rephrase this as a correlation rather than a causation.

We have rephrased the sentence to be “proton delocalization, and the resulting enhanced transient autoprotolysis, observed in PIMD simulations correlate with the much larger bandgap renormalization of ice Ih due induced by NQE, compared to water.”

5) *The authors can explicitly state that the architecture (NEP) of the revpbe0-D3 potential when first referenced as they have for the SCAN potential.*

The manuscript already has a sentence stating the architecture of the revpbe0-D3 potential but did not reference the shorthand of NEP so we have added that accordingly in the manuscript. The revised sentence reads as: “Using revPBE0-D3, we obtained a neural network potential fitted with an evolutionary algorithm (“neuroevolution potential” - NEP).”

6) *Why isn't 77 K a more relevant condition to study ice given the existence of experimental results? Wouldn't the results be expected to be different considering a lower probability of proton transfer?*

Engel et al.[1] previously estimated the effects of both temperature and proton disorder. Figure 5 of their paper finds that the band gap of bulk Ice I_h for temperatures ranging from 0 to 240 K varies only by 0.05 eV. Here we computed the bandgap of the same bulk ice system at hybrid DFT level (revPBE0-d3) at four temperatures (170 K, 200 K, 230 K, 260 K) and found that the temperature dependence of the bandgap and of the NQE renormalization is very weak between 170 and 230 K. Furthermore, while it is true that the few experimental estimates are carried out at 77 K, we chose 230 K as it is a more environmentally relevant temperature for examining ice as a solvation medium for environmental pollutants and as a catalyst for atmospheric chemistry reactions within snowpacks or clouds, as discussed on page 5 of the manuscript. As such we want to emphasize that even at higher temperature, these NQEs have a significant impact on the electronic structure of Ice I_h .

7) *How do the authors account for proton disorder in ice I_h ? This could be easily checked as meta GGA level.*

As previously discussed, Engel et al.[1] previously estimated the effect of proton disorder on the band gap, and found that the band gaps for different realizations of proton disorder have a 75 meV spread, which is much smaller than the standard deviation of our calculations. Additionally, for our Ice I_h structure we used GenIce,[2] which ensures the generation of completely randomized hydrogen-disordered networks obeying the ice rules. We have included the following sentence in the methods section of the SI “To generate our proton disordered Ice I_h system we used the GenIce[2] which ensures the generation of completely randomized hydrogen-disordered networks obeying the ice rules.”

8) *The phrase “bandgap renormalization of 1.65 eV due to NQEs using a geometry-optimized structure” is confusing. Can the authors clarify?*

What we meant by this sentence is that the bandgap renormalization with respect to a zero temperature optimized structure is 1.65 eV, which we obtained by taking the difference between a geometry-optimized structure and structures obtained from the PIGLET simulations. We have rephrased the sentence to “We find a similar bandgap renormalization with respect to a zero temperature optimized structure of 1.65 eV using the difference between a geometry-optimized structure and the band gap value obtained from the quantum DNNP@SCAN simulation at 230 K.”

9) *It would be good to elaborate a bit more on this point “The underestimation of the bandgap with revPBE0 can be in part attributed to the fact that the inverse of the appropriate fraction of exact*

exchange in the hybrid functional is more than two times larger than that of the electronic dielectric constant of water.”

A thorough discussion of the physical meaning behind the mixing parameter of hybrid functionals has been carried out in former publications.[3] We have added the following sentence to point the reader to the discussion: “Where it has been previously shown that the physical value of α can be related to $1/\epsilon_\infty$ for a given material.[3]”

10) *Fig 2 could be made more clear by using dashed lines for classical Vs quantum and just two colours.*

We agree with the reviewer and we have changed the figure accordingly.

11) *Hydrogen bonds can strengthen due to proton sharing as opposed to how is discussed in “may also stem from the weakening of hydrogen bonds due to quantum delocalization”*

Previously it was shown that nuclear quantum effects lead to two competing effects, both strengthening and weakening of the hydrogen bonds[4], in different spatial regions. Figure 5 of the reference [4], shows that for a water molecule participating in a hydrogen bond, if one of the hydrogen atoms is stretching out towards the neighboring water molecule, approaching a transient autoprotolysis event, the probability that the second hydrogen bond undergoing another autoprotolysis event is significantly reduced. Additionally, they found that for a given water molecule, if one of the hydrogen bonds is weak, or broken, there is a slight enhancement of the probability that the second donated hydrogen bond will be involved in a transient autoprotolysis event. So while we agree with the reviewer that the proton sharing may strengthen hydrogen bonds in some regions, simultaneously it is also correlated with weakening hydrogen bonds in other regions. We have added the following sentence to the manuscript “This is consistent with the known incorporation of NQEs, either strengthening or weakening of hydrogen bonds, depending on the local bonding environment.[4]”

12) *Can the authors clarify the definition of the proton transfer coordinate? The way it's defined currently, it can't have positive values. However, Fig 3 has positive values.*

We have revised the definition of the asymmetric proton transfer coordinate referring to the original paper in which it was introduced.[5]

The text now reads: “The proton transfer coordinate, defined as $v = d_{OH} - d_{O'H}$, represents the asymmetric stretch coordinate obtained from the two oxygen-shared hydrogen distances d_{OH} and $d_{O'H}$.”

Since we do not have excess protons and never observe a permanent proton transfer, it is always possible to assign the atoms to each molecule and refer to d_{OH} as the intramolecular distance and $d_{O'H}$ as the H-bonded distance, even if in the occasional fleeting proton transfer where $d_{OH} > d_{O'H}$ and v is positive.

References

- (1) Engel, E. A.; Monserrat, B.; Needs, R. J. *J. Chem. Phys.* **2015**, *143*, 244708.
- (2) Matsumoto, M.; Yagasaki, T.; Tanaka, H. *J. Comp. Chem.* **2018**, *39*, 61–64.

- (3) Marques, M. A. L.; Vidal, J.; Oliveira, M. J. T.; Reining, L.; Botti, S. *Phys. Rev. B* **2011**, *83*, 035119.
- (4) Ceriotti, M.; Cuny, J.; Parrinello, M.; Manolopoulos, D. E. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 15591–15596.
- (5) Tuckerman, M. E.; Marx, D.; Klein, M. L.; Parrinello, M. *Science* **1997**, *275*, 817–820.