Supplementary Information for Excess electrons in ice: an ab-initio study

Somesh Kr. Bhattacharya [*1], Fakharul Inam [†1] and Sandro Scandolo[‡1,2]

[1]Abdus Salam International Center for Theoretical Physics, Strada Costiera 11, Trieste, I-34151, Italy
[2]CNR-IOM "Democritos" National Simulation Center, Trieste, Italy

1 Model generation

We adopt a novel way to obtain the low density amorphous (LDA) phase of ice. Exploiting the structural similarities between liquid water, amorphous ice and amorphous silicon (a-Si) [Benmore *et al*, Phys. Rev. B **72**, 132201 (2005)], we decorated the four-folded 'www' [Wooten *et al*, Phys. Rev. Lett. **54**, 1392 (1985)] tetrahedral network of a-Si by substituting Si atoms with O atoms and placing H atoms at midway between each closest O-O pairs. The resulting structures were then relaxed to minimize the total energy and forces of at zero pressure. The calculations were performed using the SIESTA code [Soler *et al*, "The Siesta method for ab initio order-N materials simulation" , J. Phys.: Cond. Mat. **14**, 2745 (2002)] which is based on density functional theory (DFT). This code uses local orbitals and for all our calculations we used BLYP pseudo potentials and double zeta polarized basis sets optimized for water. Our LDA model consists of 64 molecules and contains perfect four fold coordination. The density obtained is 0.936 g/cm^3, compared very well with the experimental density of 0.94 g/cm^3. The pair correlation functions show very good comparison with the diffraction measurements. The first shell in the O-O pair correlation and the second broader peak is nicely reproduced. Comparing to the LDA models generated using classical potential (SPC), the widths of the first shell is much improved, while the classical models, due to the more directional interactions, show smaller widths compared to the experimental data. More details on the model generation and a comparison with other models as well as with experiments will be discussed elsewhere.

In order to obtain a range of models with different degrees of H-bond disorder, we started with four folded hydrogenated a-Si models with varying H content [Biswas *et al*, J. Phys.: Cond. Mat. **21**, 084207 (2009)]. By decorating

[*]somesh.kb@gmail.com
[†]finam@ictp.it
[‡]scandolo@ictp.it

these networks with O and H as described above, we get the LDA configurations containing varying number of H-bond defects. The a-Si:H models contain H in dispersed configuration which is suitable to obtain LDA models containing H-bond defects scattered in the network, thereby introducing local disorderness (in terms of H-bonding) into the structure.

It is important to note that all the LDA models obtained using SIESTA calculations and used in this work were further relaxed using Quantum Espresso. Upon this relaxation, the change in the pair correlation function of the LDA models is negligible. The essential parameters for relaxation are described in the main text.

2 Isosurface plots

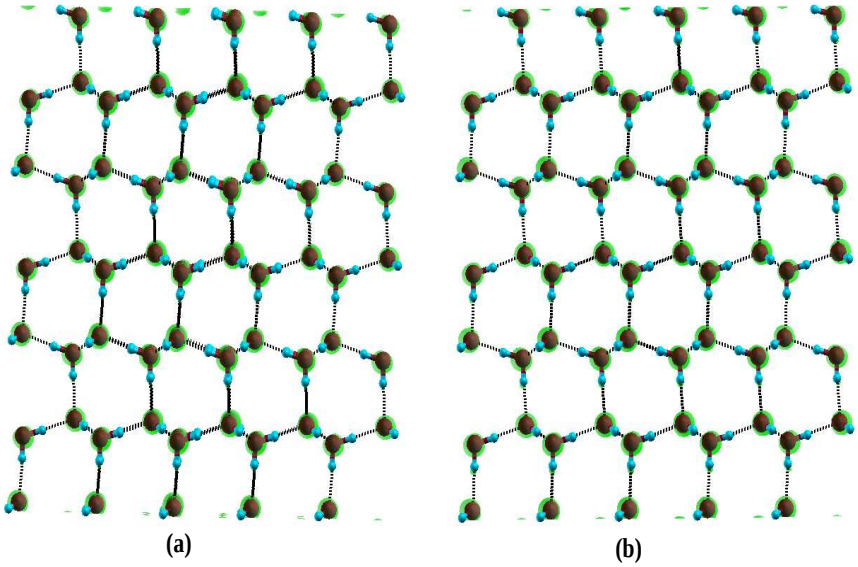

Figure 1: (Isosurface plots for (a) LUMO of crystalline ice (without vacancy) (b) Charge density of the excess electron (EE) in the bulk crystalline ice (without vacancy). The EE occupies the LUMO of the neutral system and is delocalized. Blue - H atoms, Red - O atoms. The isosurface is represented by the transparent green color. Hydrogen bonds depicted by broken lines.

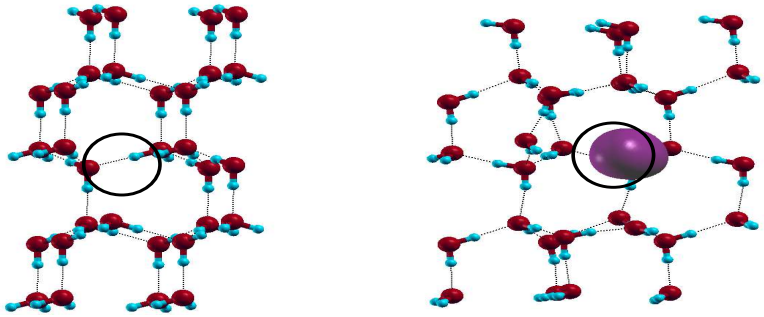

Figure 2: (a) Crystalline Ice with a vacancy. The vacancy site is encircled. (b) Isosurface plot for the EE charge density in bulk crystalline ice having a vacancy. The EE was found to be localized in the vacancy site (denoted by the circle). O atoms - red, H atoms - blue, charge density - purple. Hydrogen bonds depicted by broken lines.

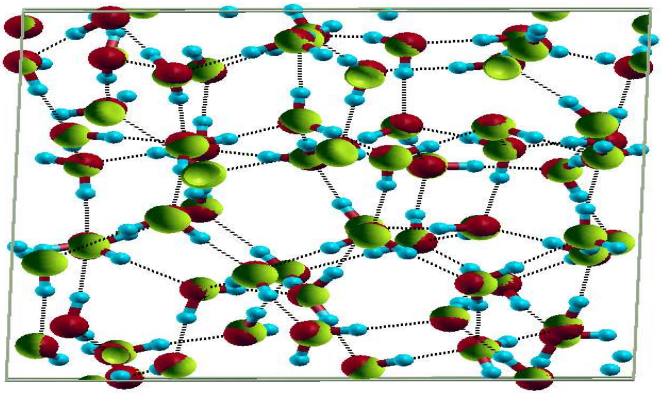

Figure 3: Charge density plot for the LUMO of the LDA neutral system. The LUMO of the neutral system in delocalized over the supercell. O atoms - red, H atoms - blue, charge density - green. Hydrogen bonds depicted by broken lines.

3 Charge density calculations

We describe here the method used to calculate the overlap between the charge density of the excess electron wave function and the charge density of the neutral molecular system. In our theoretical approach (see main paper for details) we deal with $4N_{mol}$ or $4N_{mol}+1$ states (N_{mol} being the number of molecules in the simulation box) for calculations of the neutral system or for calculations with an excess electron (EE), respectively. In both cases the first $4N_{mol}$ states are filled with 2 electrons, while the EE state is filled with one electron. We define EE density (ρ_{EE}) the charge density of the EE state. We define "paired" density (ρ_{paired}) the density constructed by summing the first $4N_{mol}$ doubly occupied states. In the case of the neutral system the paired density coincides with the total density. Our first aim is to identify and quantify the regions of space that we can consider to be occupied by a given charge density, either paired, or EE. Because wave functions and charge densities take finite values everywhere, we begin our analysis by introducing a cut off for the densities. The cut offs will allow us to determine whether a point in space is occupied by the paired and/or by the EE density.

3.1 Paired density

We begin by defining the density cut off for the paired density. This is done by considering the system with the simplest geometry, i.e. the surface of crystalline ice. We consider the geometry described in the main part of the paper. In this geometry the region occupied by the crystal is roughly 1/3 of the vacuum region, and therefore the vacuum region occupies about 75% of the total volume of the supercell. Notice that according to this definition the empty regions inside the ice slab and between the molecules are not considered as part of the vacuum. The density cut off for the paired density, $\rho_{threshold}$, is determined by computing for different values of the cut off the fraction of the total volume of the supercell where the condition $\rho_{paired} < \rho_{threshold}$ is satisfied. In practice, volumes are determined by counting the number of grid points using the same grid used for density integrals in the electronic structure calculation. N_{vac} is the number of grid points where the condition $\rho_{paired} < \rho_{threshold}$ is satisfied, and N_{tot} is the total number of points in the grid. Figure 4 shows the fraction $\mathrm{N}_{vac}/\mathrm{N}_{tot}$ as a function of $\rho_{threshold}$. The rapid change in the slope of $\mathrm{N}_{vac}/\mathrm{N}_{tot}$ around $\mathrm{N}_{vac}/\mathrm{N}_{tot} \sim 0.6 - 0.8$ is consistent with the fact that 0.75 is the fraction of empty space in the simulation cell. For $\mathrm{N}_{vac}/\mathrm{N}_{tot} = 0.75$ we find that $\rho_{threshold}$ takes the value of approximately 0.001. We therefore set to $\rho^{paired}_{threshold} = 0.001$ the value of $\rho_{threshold}$ that we will use to distinguish between regions occupied by paired charge ($\rho_{paired} > \rho^{paired}_{threshold}$) and regions that we will consider empty of paired charge ($\rho_{paired} < \rho^{paired}_{threshold}$). We also compute the fraction of paired charge contained in the region where the condition $\rho_{paired} < \rho_{threshold}$ is satisfied, i.e.

$$ratio_{charge} = \frac{\int \rho^{selected}_{pair} dV}{\int \rho_{pair} dV} \quad (1)$$

At $\rho_{threshold} = \rho^{paired}_{threshold}$ we find that the fraction of paired charge in the "empty" region is about 1% .

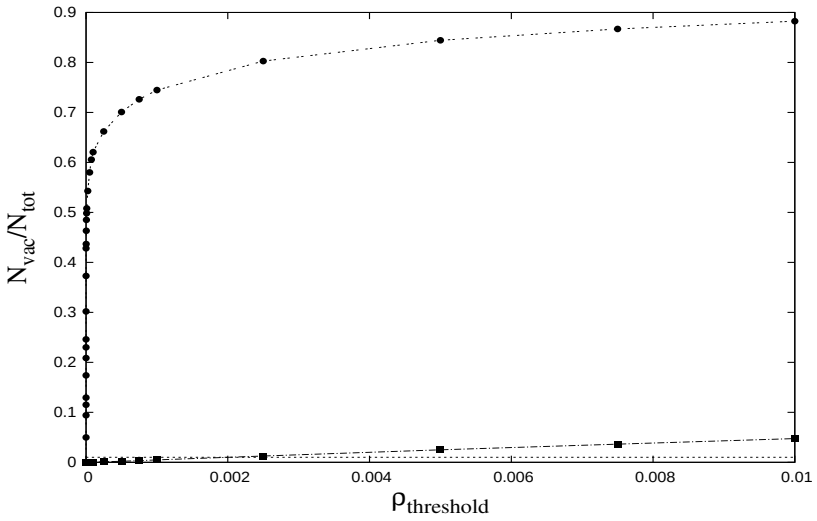

Figure 4: Plot of N_{vac}/N_{tot} (filled circles) and $ratio_{charge}$ (filled squares) (as defined in eq.1) vs $\rho_{threshold}$ for the surface geometry.

We repeated the calculations described above for the amorphous ice structure labeled as LDA-0 in the main paper. The results are shown in Figure 5. The slope of N_{vac}/N_{tot} is now smoother than in the case of the surface, indicating that the distinction between regions occupied by paired charge and empty regions is less clear. Nonetheless, using the value of $\rho^{paired}_{threshold} = 0.001$ determined above, we infer that the "empty" region occupies only 25% of the simulation cell.

3.2 Excess electron density

In order to determine the region of space occupied by the excess electron we follow a procedure similar to the one described in the previous section. We begin by defining a density cut off for the excess electron (EE) density. This is done by computing for different values of the EE density cut off the fraction of the total volume of the supercell where the condition $\rho_{EE} < \rho_{threshold}$ is satisfied. We again consider the system with the simplest geometry, i.e. the surface of crystalline ice.
Figure 6 shows that the fraction of EE charge contained in the region where $\rho_{EE} < \rho_{threshold}$ has a sharp increase in correspondence to the value of $\rho_{threshold} \sim 0.000065$. This value of the cut off corresponds to about 80% of the total EE charge. We therefore set to $\rho^{EE}_{threshold} = 0.000065$ the value of $\rho_{threshold}$ that we will use to distinguish between regions occupied by EE charge ($\rho_{EE} > \rho^{EE}_{threshold}$) and regions that we will consider empty of EE charge ($\rho_{EE} < \rho^{EE}_{threshold}$). With this definition, the volume occupied by the EE corresponds to about 14% of the total volume of the simulation cell.

The overlap between the EE charge and the paired charge is determined by using the two thresholds discussed above.

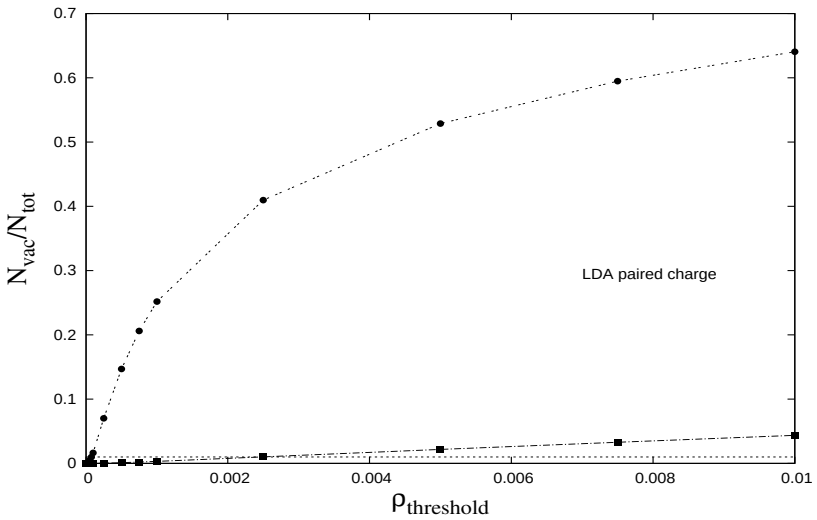

Figure 5: Plot of N_{vac}/N_{tot} (filled circles) and $ratio_{charge}$ (filled squares) (as defined in eq.1) vs $\rho_{threshold}$ for LDA-0 geometry.

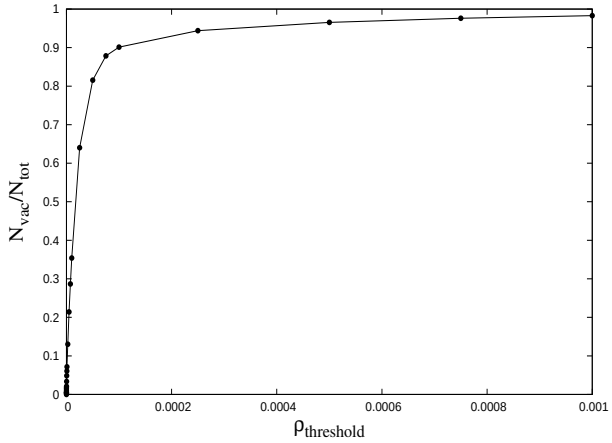

Figure 6: Plot of N_{vac}/N_{tot} vs $\rho_{threshold}$ for EE in LDA-0 geometry.