Microscopic representations of the dielectric response in ice and water

Deyu Lu[1], Hugh Wilson[1], François Gygi[2], and Giulia Galli[1]

[1]*Department of Chemistry, University of California, Davis*
[2]*Department of Applied Science, University of California, Davis*
Davis, CA, 95616, USA

The physical and chemical properties of water are of fundamental importance in numerous fields of science. *Ab initio* calculations based on density functional theory (DFT) have been shown to qualitatively account for various structural and dynamical properties of ice and water. However, excited state properties may not be evaluated satisfactorily under standard DFT, pointing at the importance of exchange-correlation effects beyond gradient approximations. Within many-body perturbation theory (MBPT), a major ingredient of the correlation effects is the screening of the electrons (holes) described by the dielectric response function. The calculation of such a response function is computationally very demanding, as it exhibits an unfavorable scaling with system size, thus preventing the study of excited state properties of large water samples and solvated molecules using MBPT.

In this talk, we present a first principle study of the static dielectric properties of ice and liquid water [1], and discuss locality properties of their respective dielectric matrices, in particular those of the lowest eigenmodes of ϵ^{-1}. We show that these locality properties can be conveniently exploited to construct approximate dielectric matrices that enable efficient calculations of quasiparticle energies within the GW approximation. In order to obtain the lowest dielectric eigenmodes, we use a newly proposed iterative approach [2], which avoids the evaluation and diagonalization of the full dielectric matrix, as well as the expensive direct summation over the unoccupied electronic states. We present results obtained for water clusters with this iterative method, and discuss the representation of the dielectric eigenmodes of water clusters with local basis functions derived from the dielectric response of the water monomer.

[1] D. Lu, F. Gygi, and G. Galli, Phys. Rev. Lett., **100**, 147601 (2008).

[2] H. Wilson, F. Gygi, and G. Galli, Phys. Rev. B, submitted.