

## Water clusters, ice and liquid: Improving *ab initio* energetics

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Water has probably been studied more comprehensively than any other substance, but its energetics remains surprisingly elusive. The properties of water clusters, ice structures and the bulk liquid are poorly reproduced by conventional density functional theory (DFT), for reasons that are still controversial. I will summarise some new approaches that we are pursuing at UCL in collaboration with colleagues in Cambridge and Bristol, focusing particularly on our recent work with quantum Monte Carlo (QMC) [1], but emphasising also the ideas of Gaussian Approximation Potentials [2]. I will show that QMC is much more accurate than DFT for the energetics of clusters and ice structures, and that it can also supply energy benchmarks for statistical samples of configurations of the bulk liquid. We are using the benchmarks to analyse the source of errors in DFT approximations and to quantify the accuracy of GAP corrections to DFT. It is becoming clear from this work that conventional DFTs struggle to describe water systems correctly because they misrepresent the subtle balance between 2-body and beyond-2-body parts of the energy.

[1] M. J. Gillan, M. D. Towler and D. Alfe, "Petascale computing opens new vistas for quantum Monte Carlo", Scientific Highlight, Psi-k Newsletter No. 103, February 2011.

[2] A. P. Bartok, M. C. Payne, R. Kondor and G. Csanyi, "Gaussian Approximation Potentials: The accuracy of quantum mechanics without the electrons", Phys. Rev. Lett., **140**, 136403 (2010).