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ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

The *ab initio* energetics of water clusters, ice and the bulk liquid: DFT meets quantum Monte Carlo

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Abstract: Water has probably been studied more extensively 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 describe 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) [1,2], but emphasising also machine-learning ideas based on Gaussian Approximation Potentials [3-5]. I will show that QMC is much more accurate than standard DFT methods for the energetics of clusters and ice structures, and that it can also supply energy benchmarks for statistical samples of configurations of thermal-equilibrium nano-droplets and the bulk liquid. We are using the benchmarks to analyse the origin of errors in DFT approximations. Our analysis shows that conventional DFT approximations suffer from important errors in both the 2-body and the beyond-2-body parts of the energy. I will show how these errors can be corrected.

[1] M. J. Gillan, F. R. Manby, M. D. Towler and D. Alfè, Assessing the accuracy of quantum Monte Carlo and density functional theory for energetics of small water clusters, J. Chem. Phys. **136**, 244105 (2012).

[2] D. Alfè, A. P. Bartók, G. Csányi and M. J. Gillan, Energy benchmarking with quantum Monte Carlo for water nano-droplets and bulk liquid water, in preparation.

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

[4] A. P. Bartók, M. J. Gillan, F. R. Manby and G. Csányi, Machine learning for predictive condensed-phase simulation, arXiv: 1302.5680 (2013).

[5] M. J. Gillan, D. Alfè, A. P. Bartók and G. Csányi, First-principles energetics of water: a many-body analysis, arXiv: 1303.0751 (2013).