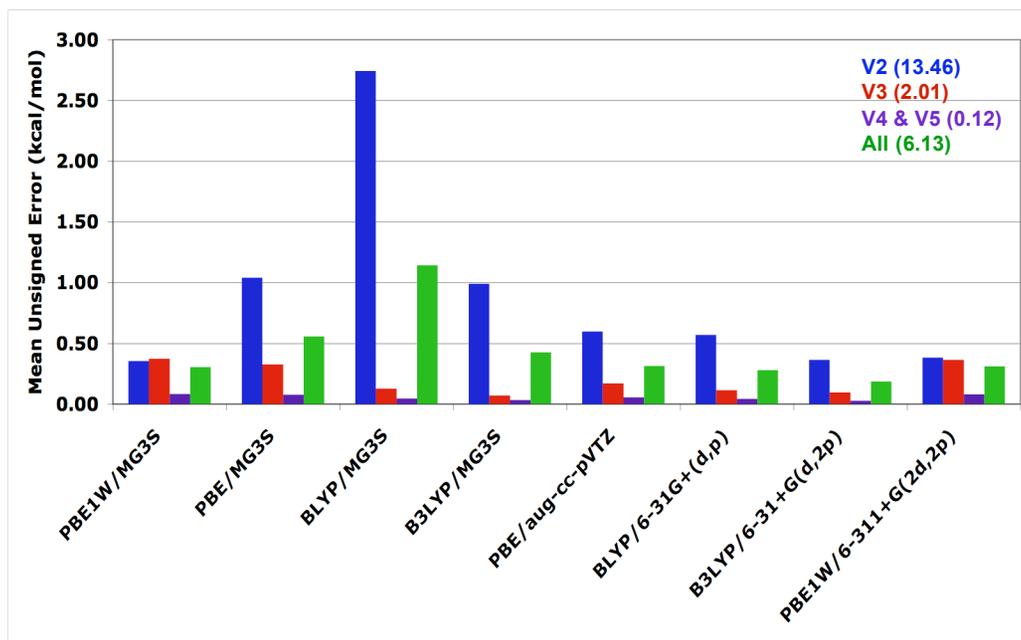


Virtual Laboratory for Earth and Planetary Materials, *VLab*

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Assessment of the Pairwise Additive Approximation and Evaluation of Many-Body Terms for Water Clusters



The ability of density functional methods to be able to correctly predict many-body terms in small water clusters may be an important measure of their success in condensed-phase simulations. We have assessed the accuracy of several density functionals commonly used in the simulation of bulk water and ice to accurately predict the many-body effects in small water clusters ranging in size from trimer to pentamer. We have found that all GGAs tested (PBE1W, PBE, BLYP) are inaccurate for predicting the many-body effects in these small clusters, and we see improved performance upon using a hybrid method (B3LYP). Despite this limitation, however, PBE1W continues to perform the best in predicting the binding energies of small water clusters, giving the lowest mean unsigned error (MUE) in the prediction of binding energies for a collection of 112 dimers, trimers, tetramers, and pentamers. We find that the magnitude of the many-body effects for small gas-phase optimized clusters are larger than those from clusters taken from the simulation of bulk water and ice. Additionally, we have noted a large basis set dependence on the performance of different density functionals, both in the prediction of binding energies and many-body terms.

Dahlke, E. E.; Truhlar, D. G. *J. Phys. Chem. B*, **2006**, *110*, 10595.

The accuracy of different density functionals depends greatly on the choice of basis set, which has implications for importing experience gained with quantum chemical basis sets into plane wave methods used in condensed phase simulations of water and ice. For an appropriate choice of basis set, the hybrid B3LYP functional performs better than any of the GGAs (PBE1W, PBE, BLYP), which all give similar results. All errors in the figure are relative to many-body terms obtained using the very accurate Weizmann-1 level of theory. The average absolute magnitude of each many-body term is given in parentheses.



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