Some Choices Are Better Than Others in Studying the Universal Solvent

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Understanding the formation of clouds and other water-based reactions involved in climate change means understanding how water behaves at the molecular, atomic, and subatomic level. Scientists recently ranked the accuracy of different equations used in a popular modeling approach, known as density functional theory

By mixing and matching choices from a buffet of 30 to 70 options, scientists are modeling water's behavior in surface and subsurface reactions and in heterogeneous atmospheric processes such as the formation of clouds. But, how accurate are the models built with this

approach, known as density functional theory (DFT)?

Scientists at Pacific Northwest and Argonne National Laboratories and the University of Buffalo ranked the accuracy of 7 different functionals or mathematical expressions used in DFT. Their article quickly became a popular download from the Journal of Chemical Physics.

The ubiquitous nature of water means that scientists regularly model the behavior of clusters of water molecules in different environments, such as around charged species and at environmental interfaces, in biomass fuel reactors and in processes occurring in polar stratospheric clouds. Using the results of this study, scientists can better judge the accuracy of the water models they create with fast, inexpensive DFT calculations.

The team began by obtaining highly accurate data on the polarizability of a collection of up to 12 water molecules. Polarizability refers to how the electron cloud of an atom or a molecule is distorted as a result of its response to an external electric field. These data served as the "gold standard" for benchmarking various DFT functionals. They obtained this data using a computationally intensive and expensive process known as the coupled cluster level of theory.

Next, they compared the impact of selecting 7 different functionals for the DFT calculations. The study demonstrated that HCTH performed quite well, as did PBE0. Both provided accurate results about the polarizability of water molecules. Using these benchmark results, scientists can now better judge the accuracy of their water models.

In performing the gold standard and the DFT calculations, the team used NWChem, a computational chemistry package that runs on supercomputers. This work was done as part of a Computational Grand Challenge proposal using the Chinook supercomputer at the Department of Energy's EMSL, a national scientific user facility at PNNL.

While HCTH and PBE0 offer accurate answers, the scientists want to further improve the accuracy of DFT. These parameters should provide accurate answers without adding excessive, expensive computational time. So, the scientists are continuing to investigate the theoretical requirements needed to accurately predict the properties of the planet's most common solvent: water.

More information: Hammond JR, N Govind, K Kowalski, J Autschbach, and SS Xantheas. 2009. "Accurate dipole polarizabilities of water clusters n=2-12 at the coupled-cluster level of theory and benchmarking of various density functional." Journal of Chemical Physics 131, 214103.

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