Test of QTP Family of Density Functions to EA-AOM -CCSD for Electron Affinities

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As the world of chemistry progresses, it becomes increasingly necessary to define textbook values for basic molecular properties. Running CCSDTQ for every molecule is possible, and would grant highly accurate results, but would be extremely costly and time inefficient. Density functional theory provides a cheaper, quicker estimate, but is not always accurate to the same extent as correlated methods are. My research investigates which DFT functional can most closely emulate CCSD results for electron affinity calculations of small organic molecules.

Using the ACESII program package, we performed EA-EOM-CCSD calculations with an augmented cc-pVTZ basis. We also compiled LUMO EA values from calculations with six different DFT functionals, all of which were performed using the program ORCA. The calculations using these six DFT functionals- CAM-QTP00, CAM-QTP01, CAM-QTP02, LC-B3LYP, WB97X, and CAM-B3LYP- were all performed with the aug-cc-pVTZ basis set.

Both the EA-EOM-CCSD and DFT functional calculations were performed on a set of 62 small organic molecules from D.S. Ranasinghe's benchmark set. The geometries for these molecules, referred to in Ranasinghe's work as the CGB set, were optimized at the CCSD(T) level with an aug-cc-pVTZ basis set. Note that the benchmark set was originally intended for IP calculations and was not altered in any way for our EA calculations- thus giving an unbiased treatment of our benchmark set of molecules. Of the 62 molecules, we were able to converge 38 for CCSD-EA-EOM, of which 33 were plotted against the DFT functionals to find the coefficient of determination (R^2) for each functional.

Results demonstrated that the QTP00 functional was able to predict the CCSD EA-EOM results most accurately for small organic molecules. When plotted against the CCSD results, QTP00 had an R^2 value of 0.9465, followed closely by QTP02 at 0.9453. QTP01, CAM-B3LYP, WB97X, and LC-B3LYP had R^2 values of 0.8826, 0.7621, 0.7245, and 0.3178, respectively.

Further research should be conducted on the experimental electron affinities of these small organic molecules, as very few experimental numbers are available in publication, and the only way to know if any of these functionals are truly accurate in their predictions would be to compare them to experimental values. There were also five molecules of our benchmark set for which EA-EOM predicted a bounded molecule, but all DFT functionals predicted an unbounded molecule, and further investigation is needed to determine why this was the case.