Modeling Transition States in S_n2 Identity Reactions; a Comparison of Basis Sets and Functionals.[1]

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Rather than solving the Schödinger equation, density functional theory (DFT) uses electron densities to optimize molecular structures and determine the enthalpy of a reaction. In this work use DFT to examine nucleophilic substitution of halides in methyl halides, which can be described by the reaction:

$$X^- + CH_3X \rightarrow XCH_3 + X^-$$

By studying the energetics of this reaction in the gas phase when X = F, Cl and Br, we were able to compare the accuracy of several basis sets and functionals. Even the smallest augmented basis set in the correlation consistent family (aug-cc-pvdz) performed better than the split valence basis 6-31G. 19 functionals were tested, including B3LYP, HFS, B1LYP, and mPW1PW91. The minimum energy path for the identity closely approached results for highly accurate *ab initio* calculations using the W1 composite thermochemistry model – three different functionals closely reproduced the W1 evaluations. These three functionals were the same for all three halogens. B1B95 yielded the best results for all three halogenic identity reactions, although the three halogens have very distinct properties. Larger basis sets were also tested, without significant improvement in accuracy; that is an indication that DFT itself may be the main limiting factor for the accuracy of these calculations.

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