LOCALLY DENSE BASIS SETS FOR ACCURATE THERMOCHEMISTRY

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The use of locally dense basis sets (LDBS) has gained wide acceptance in the field of NMR shielding calculations. This method allows for the accurate determination of properties, for centers of interest in larger molecules, by treating them with a large basis set while a smaller basis set is used for the rest of the molecule. The required CPU time is greatly reduced by using LDBS while very little accuracy is lost [1].

We have recently examined the use of locally dense basis sets, in conjunction with the B3LYP method, for the determination of bond dissociation energies (BDE) and electron affinities (EA) of large molecules (for example, α-tocopherol with 81 atoms). Our method involves assigning basis sets of various sizes to regions of a molecule based on chemical understanding of the various structural features of the subject species. Our current results indicate that BDEs and EAs determined by our approach (LDBS + B3LYP) are remarkably insensitive to these assignments.

We will present the results of test calculation which illustrate the utility of our method and discuss some of the implications of our findings.

1. D.B. Chesnut and K.D. Moore, J. Comput. Chem, **10**, 648, 1989.