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THEORETICAL STUDIES OF GROUP IVA AND GROUP IVB CHEMISTRY

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Several new developments in the effective fragment potential (EFP) and the fragment molecular orbital (FMO) methods have been accomplished. A new EFP charge transfer (CT) interaction energy was derived and implemented in GAMESS. The new CT approach, based on quasi-atomic molecular bond orbitals, cuts the time required for this term by a factor of two, with little loss in accuracy. The analytic gradient was derived and implemented as well, so one can optimize geometries and determine reaction paths. The R(-7) dispersion terms was also derived and coded. While most workers ignore the odd power dispersion terms, these terms can be very important in anisotropic situations, such as highly viscous liquids and on solid surfaces. We have also developed an integrated FMO-EFP method called the effective fragment molecular orbital (EFMO) method. We have shown that the EFMO method is both faster and more accurate than FMO. Fully analytic EFMO energy gradients have been partly completed. In

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Several new developments in the effective fragment potential (EFP) and the fragment molecular orbital (FMO) methods have been accomplished. A new EFP charge transfer (CT) interaction energy was derived and implemented in GAMESS. The new CT approach, based on quasi-atomic molecular bond orbitals, cuts the time required for this term by a factor of two, with little loss in accuracy. The analytic gradient was derived and implemented as well, so one can optimize geometries and determine reaction paths. The R(-7) dispersion terms was also derived and coded. While most workers ignore the odd power dispersion terms, these terms can be very important in anisotropic situations, such as highly viscous liquids and on solid surfaces. We have also developed an integrated FMO-EFP method called the effective fragment molecular orbital (EFMO) method. We have shown that the EFMO method is both faster and more accurate than FMO. Fully analytic EFMO energy gradients have been partly completed. The analytic gradients will be completed in the next year. Once these gradients are completed, one can do molecular dynamics simulation with the essentially ab initio EFMO method. In collaboration with the Rappe group, we used the EFP and second order perturbation theory (MP2) to help explain the experimental results of the Fayer group on phenol migration dynamics. An exhaustive computational study of hydrazine decomposition was performed using both MP2 and coupled cluster methods. This study, which was prompted by the use of hydrazine as a high energy fuel, completely mapped out the competing hydrazine decomposition pathways. This work was a true tour de force. An invited review on fragmentation methods is in press in the very prestigious journal Accounts of Chemical Research. Also in press is a report on the solvated electron. This is a very important work, because it demonstrates that local orbital methods, such as the cluster in molecule (CIM) method can be very effective in studying the solvated electron problem. The solvated electron is often thought of as a highly delocalized problem, but our work demonstrates that this is not true.

A thorough study of the isomers of the water hexamer and the Ar hexamer was completed. This study compared the predictions of coupled cluster theory, CCSD(T), MP2, EFP, Hartree-Fock (HF) and density functional theory (DFT) with several density functionals. Ad hoc dispersion corrections (-D) were added to both the HF and DFT calculations. It was shown that the EFP method is in best agreement with the high-level benchmark CCSD(T) calculations, even better than the MP2 theory. Indeed, MP2 predictions get worse when the basis set is improved. HF and DFT predictions of the water hexamer binding energies are generally very poor. When the –D correction is included, both HF-D and DFT-D are improved. The performance of HF-D is especially encouraging since one can think of HF-D as an inexpensive alternative to MP2.

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