New Developments in Fragment-Based Quantum Chemistry

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We describe several fragment-based approaches with the potential to extend quantum chemistry to very large systems. The first of these is an "extended" version of symmetry-adapted perturbation theory (XSAPT) that can be applied to compute benchmark-quality intermolecular interaction energies in noncovalent clusters and assemblies.[1] This method is both more accurate and less costly than supramolecular density functional theory. The XSAPT method naturally includes nonadditive polarization effects and we have recently extended it to include nonadditive many-body dispersion (MBD) as well.[2] The resulting XSAPT+MBD method provides ~ 1 kcal/mol accuracy in calculations with hundreds of atoms and thousands of basis functions. In a second project, we have developed a general framework for fragment-based quantum chemistry that we call the generalized many-body expansion (GMBE),[3,4,5] which we have recently extended to *ab initio* molecular dynamics simulations. By introducing a variational framework for the GMBE, we derive a fragment-based method that preserves the variational nature of the self-consistent field method (SCF), even when the subsystem SCF calculations are embedded in an electrostatic (point-charge) representation of the entire system.[6] This formalism naturally leads to charge-response contributions to the Fock matrix (which have often been neglected in practice), although solution of coupled-perturbed SCF equations is not required. We show that several other fragment-based methods that do not consider the charge-response contributions to the analytic gradient result in catastrophic failure of energy conservation in fragment-based *ab initio* molecular dynamics simulations.

References

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