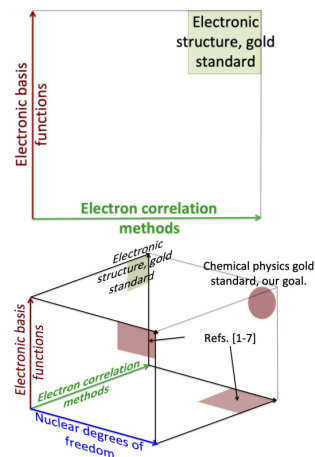


# Graph-theoretic methods for automated and adaptive many-body expansions: applications to gas- and condensed-phase AIMD, and potential surface calculations for quantum nuclear dynamics

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We present[1–7] a graph theoretic approach to adaptively compute many-body-approximations in an efficient manner to perform (a) accurate post-Hartree-Fock AIMD at DFT cost for medium to large sized molecular clusters, (b) hybrid DFT electronic structure calculations for condensed phase simulations at the cost of pure and gradient-corrected density functionals, (c) reduced cost on-the-fly basis extrapolation, where we can compute AIMD trajectories accurate to 6-311++G(2df,2pd) with computational effort commensurate with 6-31+G(d), for both condensed phase as well as gas-phase calculations, (d) accurate post-Hartree-Fock level potential energy surfaces at DFT cost for quantum nuclear effects. The salient features of our approach are ONIOM-like in that, (a) the full system (cluster or condensed phase) calculation is performed at a lower level of theory (semilocal, or pure, DFT for condensed phase or hybrid DFT for molecular systems), and (b) this approximation is improved through a correction term that captures all many-body interactions up to any given order within a higher level of theory (hybrid DFT for condensed phase, CCSD or MP2 for cluster), combined through graph theoretic methods. Specifically, a region of chemical interest is coarse-grained into a set of nodes, or vertices, and these nodes are then connected to form edges based on a given definition of local envelope (or threshold) of interactions. The vertices and edges together define a graph, which forms the basis for developing the many-body expansion. The methods are demonstrated through (a) *ab initio* dynamics studies on protonated water clusters and polypeptide fragments, (b) potential energy surface calculations on one-dimensional water chains such as those found in ion-channels, and (c) conformational stabilization and lattice energy studies on homogeneous and heterogeneous surfaces of water with organic adsorbates using two-dimensional periodic boundary conditions.



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