Designing a coupled cluster method based entirely on T_2

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Development of cheap and accurate model chemistries to describe strong, static correlation continues to be an active field of research. An accurate accounting for this type of correlation is necessary in a myriad of important physical phenomena, and seems to predominantly involve electron-pair interactions. On the other hand, a truly robust method should come adequately equipped to handle dynamic electron correlation. In this context at least, it is well-documented that coupled cluster theory is a “gold standard” in quantum chemistry.

With this in mind, we seek ways to naturally and economically account for quadruple (T_4), hextuple(T_6), all the way up to 2n excitations within a coupled cluster doubles (CCD) framework. These high-order, connected clusters can be conveniently obtained via the adjoint of T_2, raising the possibility for an “ultimate” T_2 method as the foundation for correlated theory. Inclusion of these are justified by the idea of “factorized quadruples”, derived from the factorization theorem of perturbation theory. As a consequence, significant reductions to the error are achievable at the expense of manageable increases to the algorithmic complexity. We showcase the efficacy of these ideas on small model systems.