

A seniority-based analysis of coupled-cluster doubles

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While coupled-cluster theory at the CCD or CCSD level can accurately describe systems in which the dominant contribution to the electron correlation is mostly dynamic, it fails to describe cases dominated by static or non-dynamic electron correlation. However, static correlation can be captured using seniority zero wave functions, in which all electrons are paired. Seniority zero CCD (pCCD) can accurately reproduce results from the seniority zero doubly occupied CI (DOCI), at much less computation effort, given that one uses the DOCI pairing scheme. Since the pCCD wave function is not invariant to the choice of pairing scheme, one needs to find a basis that can reproduce DOCI results without the need to do DOCI calculations. We explore the contribution from different seniority sectors to the correlation energy at the CCD level (which includes seniority zero, two, and four) and their dependence on the pairing scheme in use. By analyzing the role of different pairing schemes in terms of seniority, we gain insight into the pairing needed for pCCD. Moreover, we explore ways to enlarge the capability of CCD to account for strong correlation by freezing the pair amplitudes prior to the calculation of the other seniority sectors.