Calculations on Small Test Systems Employing Multi-Reference Coupled-Cluster Schemes

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Previously described Multi-Reference Coupled-Cluster (MRCC) schemes (namely SRMRCC [1], RMRCC [2] and MRexpT [3]) have been applied to the hetero-nuclear LiH system and the H4 model system. The qualities of the energy expectation values and the wave-functions have been investigated as a function of the internuclear distance, respectively. The set up of the above mentioned MRCC ansätze will be briefly revisited and discussed with a focus on their intrinsic relationships and their properties. The results of the Coupled-Cluster calculations are discussed in comparison to full configuration interaction as an exact method concerning the given many-particle basis set. A focus is set on near-degeneracy and degeneracy problems such as the D_{4h} geometry in H4 since the treatment of these states is the major intention for the set up of multi-reference schemes. It will be shown that the RMRCC and SRMRCC implementations suffer from inherently symmetry broken wave-functions and are very sensitive to changes in the Fermi vacuum, while MRexpT provides reasonable results although it is neither valence- nor core-valence connected [4].

Literature:

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