Investigation of the Impact of Different Terms in the Second Order Hamiltonian on Excitation Energies of Valence and Rydberg States[*]
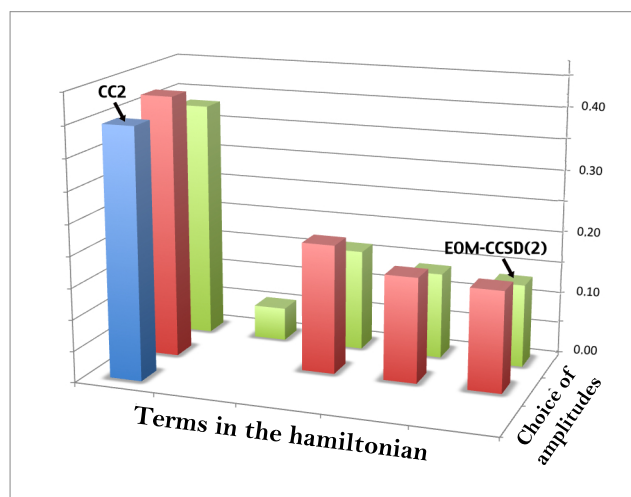
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Describing electronically excited states of molecules accurately poses a challenging problem for theoretical methods. Popular second order techniques like Linear Response CC2 (CC2-LR) or EOM-CCSD(2) often produce results that are controversial and are ill-balanced with their accuracy on valence and Rydberg type states. In this study, we connect the theory of these two methods, and establish a series of intermediate variants. The accuracy of these on excitation energies of singlet valence and Rydberg electronic states is benchmarked on a large sample against high-accuracy results including triple excitations.

The results allow the investigation of the role of individual terms of the second order similarity transformed Hamiltonian, and the reason for the bad performance of CC2-LR for Rydberg states. We also clarify the importance of the $\hat{T}_1$ transformation employed in the CC2 procedure, which is found to be very small for vertical excitation energies.