

How accurate are Coupled-Cluster methods for excited states? A systematic study for valence, Rydberg and Charge Transfer states, including vertical excitation energy and potential energy surfaces.

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Excited states are important in many fields of chemistry and even biology. Theoretical investigation of the underlying phenomena is essential for both understanding and quantitative modeling of these processes. The involved systems are often large and the mechanisms are complicated, therefore the demand on theoretical methods is two-fold: it should be reasonably cheap and (very) accurate. One of the complications from the theoretical point of view is that the wave functions of excited states, unlike those of ground states, are very diverse: open shells with varying number unpaired electrons, Rydberg and Charge Transfer states or (near) degeneracies impose quite different requirements on the theoretical model.

In this talk the performance of Coupled-Cluster type methods will be discussed. This choice can be justified by the hierarchy of Coupled-Cluster methods which enable the control (though not independently) on both accuracy and cost. After reviewing the quite extensive literature of benchmark studies on vertical excitation energies of valence excited states, it will be examined whether the same accuracy pattern applies for Rydberg and Charge Transfer states. Finally we widen the scope towards potential energy surfaces, since we believe that the accuracy of the vertical excitation energy does not necessarily mean that the shape and topology of the potential energy surfaces are also reliable.

It is hoped that this comprehensive study can serve with some useful conclusions and help selecting the appropriate method for studying interesting chemical and biological phenomena.