

Breaking bonds with approximate coupled cluster methods

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Abstract

Accurate potential energy surfaces for bond-dissociation, particularly when multiple bonds are involved, are difficult to obtain through current ab-initio methods. Their accurate description requires the use of the most precise of the available methods and consequently the most computationally expensive ones as well. Many of these systems are considered to be 'quasi-degenerate' at stretched geometries and hence sophisticated multi-reference methods based on CI or CC theory are prescribed. To obtain a more straightforward and cheaper alternative, effort has been made to find simpler approximation to the single reference coupled-cluster theory that seem to overcome its limitation. Their success has been rationalized in terms of the indirect inclusion of higher excitation effects particularly quadruples. A number of such approximate CC methods exist such as ACCD, ACP-D45, ACP-D14, 2-CC and p-CCSD. A new addition to this growing list is the Distinguishable Cluster approach based methods: DCD and DCSD. We apply all of these approximate CC methods to different bond-breaking scenarios: triple bond in N_2 and CO, double bond in $H_2C=CH_2$ and $H_2C=SiH_2$ and so on. We try to rationalize why some of these methods work, predicting correct qualitative features of the potential energy curves (PEC), while others do not and have the same fallacies as the general coupled cluster method limited to singles and double excitations, CCSD.