A Second-Order Optimisation Approach to Configurational State Functions

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Bond breaking is a ubiquitous occurrence in chemistry, yet it remains a challenging process to describe by computational methods. A prototypical example would be the failure of Restricted Hartree—Fock theory to describe bond breaking as it cannot describe open-shell configurations.

We have demonstrated in a recent work that a small number of valence states is sufficient to describe bond breaking. These valence states have open-shell configurations and Configuration State Functions (CSFs) are natural representations for them. CSFs are constructed from an underlying set of molecular orbitals, and the quality of these CSFs depend on these orbitals. Throughout the process of bond breaking, different orbitals (and hence CSFs) would be required to describe the process. However, figuring out the orbitals required is not trivial.

In this work, we explore the possibility of using a second-order optimisation scheme to optimise the orbitals used. We demonstrate that this method can produce CSFs which gives a good qualitative description of bond breaking and can serve as good reference functions for other sophisticated electronic structure approaches.