Analytic Gradients for Selected Configuration Interaction: Development and Applications

Jeremy P. Coe[1]
[1] Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

C18

Selected configuration interaction (CI) approaches iteratively build up a compact wave-function by repeatedly adding and removing configurations based on certain criteria. They are increasingly of interest partly due to their ability to cope with multireference problems without requiring an active space to be chosen.

To efficiently use these methods for geometry optimization then analytic energy gradients are crucial. However, unlike CASSCF or CISD, all pairs of orbitals in principle need to be considered when implementing analytic gradients for selected CI. This may be expected to lead to numerical problems when there are (near) degenerate orbitals, due to $(\epsilon_i - \epsilon_j)^{-1}$ terms arising from the coupled perturbed Hartree-Fock equations. I will present how this can be overcome and demonstrate that selected CI can give highly accurate analytic gradients using just a small fraction of the full configuration interaction (FCI) space [1]. Fig. 1 shows that selected CI analytic gradients for trigonal planar ammonia are practically indistinguishable to FCI despite only using around 8000 determinants compared with the FCI space of about a quarter of a million determinants. I will also discuss progress building on this work to calculate non-adiabatic couplings and optimize geometries.
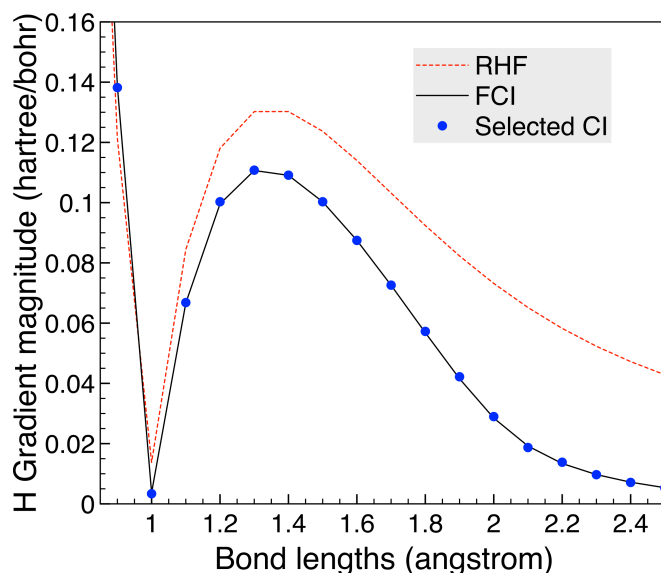

Figure 1: Magnitude of the analytic gradient vector for an H atom in trigonal planar ammonia using 6-31G.

[1] J. P. Coe, J. Chem. Phys., **19** (2023), 874.