Coupled Cluster methods for predicting molecular structures and X-ray spectra

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Development of coupled cluster (CC) methods is of great interest as they are considered the most efficient for describing dynamical electron correlation for ground states dominated by a single determinant[1]. Over the past decades algorithmic and hardware improvements have made this type of calculations increasingly feasible. Particularly CC methods including double excitations approximately (CC2[2]) or in full (CCSD[3]) are of interest, since they generally yield results of high accuracy at a reasonable computational cost.

The starting point of any quantum chemical calculation is a molecular geometry. In some cases experimental geometries are available, however this is often not the case, and instead the equilibrium structure must be calculated. This is routinely determined theoretically by way of a geometry optimization, for which molecular gradients are required. We present a new efficient implementation of CCSD gradients for both the ground and excited state[5]. Our implementation is based on Cholesky decomposition of the electron repulsion integrals[6,7], and we show that less than 10% of the calculation time is spent determining the molecular gradients, when performing a geometry optimization. In addition, when utilizing our code, a ~50% decrease in computation time for geometry optimizations is observed compared to similar implementations in other codes. While this significant speedup is largely attributed to the efficiency of the CC code, the small fraction of time spent calculating the gradients highlights the efficiency of our implementation.

Today, the field of X-ray science is of particular interest and has been developed extensively both experimentally and theoretically. We show applications of the CCSD methods in this field for predicting not only XAS spectra to analyze a new experiment on oxazole[8] using existing implementations in Q-Chem [9] and Dalton[10], but also RIXS spectra using our own new implementation, which unlike the Q-Chem implementation[11] does not require the use of frozen core.

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