Analytic Gradients in Coupled-Cluster Theory Including a Perturbative Treatment of Relativistic Effects

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For molecules containing only light elements scalar relativistic effects can be efficiently treated via first-order perturbation theory. Calculations of the corresponding mass-velocity (MV) and Darwin (D) contributions are easily accomplished using analytic first derivative techniques. The analytic evaluation of gradients for the relativistic correction, for example needed in geometry optimizations, requires further differentiation with respect to nuclear displacements, and thus is possible using analytic second derivatives.

In this work, we present a scheme to compute energy gradients (i.e., forces) including relativistic MVD corrections within coupled-cluster (CC) theory, thereby exploiting our analytic CC second derivative code. Examples are given to demonstrate the influence of relativistic effects on computed equilibrium geometries.