Explicit Analytical OSV-MP2 Energy Gradients for Molecular Dynamical Properties

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Abstract:

In several limits of approximation, an efficient low-scaling hierarchy of coupled cluster (CC) electronic structure methods has been established, such as the alternatives within the framework of projected atomic orbitals, orbital-specific-virtual (OSV), pair-nature-orbital (PNO) and so on. These methods have been demonstrated to often achieve chemical accuracy with significantly reduced CC computational cost by orders of magnitude, and applied to treat systems containing hundreds of atoms as well as condensed materials. The success of these high-level low-scaling electronic structure methods in computing molecular static properties opens up a new perspective for us to think in new ways to compute molecular dynamical properties by making similar efficiency and accuracy to those of static calculations. Along this line, we are developing an algorithm to compute the explicit analytical gradients towards the OSV-based hierarchy of energy functionals, starting with the second-order Møller–Plesset perturbation (OSV-MP2) method. Here we consider the explicit relaxation of perturbed OSV orbitals that are required to be the eigenvectors of the perturbed MP2 diagonal amplitudes. In this presentation, we will have a discussion on (1) the algorithm and implementation with an analysis of formal computing complexity, (2) formal issues and properties of both OSV and hybrid PNO orbital response vectors, (3) the numerical assessment of OSV-MP2 structure optimization for a test set of molecules, and (4) a proof-of-principle demonstration of the low-scaling ab-initio molecular dynamics simulation driven by OSV-MP2 forces.