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MCSCF/FQ Analytical Nuclear Gradients: A Novel Methodological Development for Multireference Multiscale Modeling

Multiscale approaches are valuable methods for accurately describing molecules embedded in complex environments, such as solutions. Among them, the Multiconfigurational Self-Consistent Field/Fluctuating Charges approach (MCSCF/FQ) [1] combines a multireference quantum mechanical method [2] with the FQ polarizable force field [3,4]. This combination captures the qualitative behavior of multireference systems and processes within their environment (e.g., aromatic molecules in solution, photochemical processes), where commonly used single-reference methods, such as TD-DFT, often fail. In addition, the atomistic and polarizable nature of FQ provides an accurate description of solute-solvent interactions, explicitly accounting for their mutual polarization. In this work, the MCSCF/FQ model has been extended to calculate analytical nuclear gradients, significantly enhancing the versatility of the method [5]. This development enables tasks such as geometry optimizations, vibronic spectra computations, and QM/MM molecular dynamics simulations. The MCSCF/FQ analytical nuclear gradients have been implemented in the OpenMolcas software [6] and validated against numerical gradients. As an illustrative application, vibronic spectra of aromatic molecules in aqueous solutions have been computed (Figure 1). Results demonstrate an accurate reproduction of the experimentally observed spectral profiles and relative intensities, highlighting the capability of the MCSCF/FQ approach to capture both the multireference nature of the solute and the solute-solvent interactions.

Figure 1. (Left) Representative snapshot of benzene in aqueous solution. (Right) Vibronic spectra comparison: computed with the CASSCF(6,6)/FQ method (top) and experimental data from Ref. [7] (bottom).

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