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Modeling vertical excitation energies in solution using the Density matrix renormalization group/Fluctuating charges approach

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The investigation of electronic transitions in solution is a useful tool to gather information on systems involved in important biological or chemical processes. However, solvated systems are composed of a very large number of atoms. Therefore, from a computational point of view, a reasonable way to address this is to resort to multiscale modeling [1,2]. Among these methods, hybrid Quantum Mechanics (QM)/Molecular Mechanics (MM) methods have proven to be particularly successful [3,4] because they are capable of describing specific solute-solvent interactions, such as hydrogen bonding patterns, that can play a role in shaping spectroscopic signals [5]. Furthermore, many interesting solvated systems comprise solute with complex electronic structures, e.g. conjugated systems, chromophores in photosensitive proteins or transition metal enzymes. These complex electronic structures need to be described by an accurate multiconfigurational QM approach. To this purpose, we present a QM/MM strategy based on the coupling of the Density matrix renormalization group (DMRG) method [6,7] to the Fluctuating Charges (FQ) force field (DMRG/FQ) [9]. This is based on the framework of our recent CASSCF/FQ [8] method and permits treating large solute molecules using active spaces of more than 20 electrons in 20 orbitals. The resulting DMRG/FQ method is then applied to the calculation of vertical excitation energies and solvatochromic shifts of a set of molecules in solution. A detailed comparison to reference and experimental data is made. This work paves the way for future applications on biological systems.

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